Hitachi Zosen NOx Flue Gas Treatment Process
Volume 2. Independent Evaluation

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Prepared for

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Research Triangle Park, NC

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16 ABSTRACT The report gives results of an independent evaluation of the Hitachi Zosen (HZ) NOx flue gas treatment process, one of two selective catalytic reduction (SCR) of NOx with ammonia processes (pilot-scale tested under EPA sponsorship) treating flue gas slipstreams from coal-fired boilers. Test results show that the process can reduce NOx emissions by 90%. Initial tests resulted in plugging of the catalyst. But a new catalyst with larger gas passages was tested: it operated for 5500 hours without any signs of plugging. Results of an energy analysis indicate that the HZ process energy requirements are 0.3% of the boiler's capacity. Process costs were estimated based on the pilot plant test results. Estimated capital investment and annual revenue requirements for the HZ process are $44/kW and 2.91 mills/kWh, respectively. These costs are slightly lower than previous estimates for the process.

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# ABSTRACT

Nitrogen oxide emissions from stationary sources may be reduced by 80 to 90 percent through the application of selective catalytic reduction (SCR) of $NO_x$ with ammonia. In the interest of furthering the development of this technology, EPA sponsored pilot scale tests of two SCR processes treating flue gas slip streams from coal-fired boilers. One of the processes tested was the Hitachi Zosen (HZ) process. The results of an independent evaluation of the pilot plant tests of the HZ process show that the process is capable of reducing $NO_x$ emissions from a coal-fired boiler by 90 percent. Initial tests resulted in plugging of the catalyst. But a new catalyst with larger gas passages was tested and it operated for 5500 hours without any signs of plugging. Results of an energy analysis indicates the HZ process energy requirements equal 0.3 percent of the boiler's capacity. Process costs were estimated based on the pilot plant test results. Estimated capital investment and annual revenue requirements for the HZ process are $44/kW and 2.91 mills/kWh respectively. These costs are slightly lower than previous estimates for the process.

SECTION 1

SUMMARY

1.1   INTRODUCTION

Selective catalytic reduction (SCR) of $NO_x$ with $NH_3$ is capable of reducing $NO_x$ emissions by 80 percent or more.  As such, SCR represents the most effective process available for controlling stationary source $NO_x$ emissions.  For a utility application of SCR, a catalytic reactor is located between the economizer and air preheater sections of the boiler.  At this location the flue gas temperature ranges from 300 to 400°C (570-750°F) which is optimum for the catalytic activity.  Ammonia is injected into the flue gas upstream of the catalyst and reacts with $NO_x$ on the catalyst surface to form elemental nitrogen and water.

Most SCR processes were developed and are being operated commercially in Japan, primarily on gas- and oil-fired sources.  However, in the U.S., SCR systems are now being installed on a limited basis.  The most notable application is a demonstration system that is being constructed to treat one-half of the flue gas from Southern California Edison's 215 MWe Huntington Beach Unit No. 2 (an oil-fired boiler).  The operation of this system is expected to establish SCR as a commercially available technology for oil- and gas-fired sources in the U.S.

In Japan, development efforts are currently aimed at applying SCR to coal-fired sources.  To date, most of the SCR process vendors in Japan have operated pilot units on slip-streams from coal-fired boilers.  In addition, there are now four full-scale SCR systems treating flue gas from coal-fired boilers with another eight units scheduled for start-up in 1982 and 1983.  These development

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efforts are rapidly establishing SCR as commercially available technology for controlling $NO_x$ emissions from coal-fired sources in Japan.

The transfer of SCR technology from Japan to the U.S. for coal-fired applications presents a potentially significant problem. Since most coal-fired boilers in the U.S. operate ESP's located downstream of the air preheater, a typical SCR application would expose the catalyst in the reactor to the full particulate concentration from the boiler. Although tests have been conducted in Japan in which the catalyst was exposed to high particulate concentrations with no adverse effects, the differences in the composition of particulates from U.S. and Japanese coals could impact SCR operation.

In an effort to further the development of SCR technology and to determine how differences between Japanese and U.S. coal/particulate properties impact the performance of SCR processes, EPA has sponsored pilot scale (0.5 MW equivalent) tests of two SCR systems. One of the SCR systems tested was the Hitachi Zosen (HZ) process. The HZ pilot plant processed a flue gas slipstream from a coal-fired boiler. The contractor responsible for the design and operation of the pilot plant was Chemico Air Pollution Control Corporation (now General Electric Environmental Services Corporation), which is the North American licensee for the HZ process. Chemico was also responsible for collection, evaluation, and reporting of the test data.

The primary objectives of the pilot plant test program sponsored by EPA were: (1) to demonstrate the ability of the HZ process to achieve a 90 percent reduction in $NO_x$ emissions, and (2) to determine the long-term impacts on catalyst performance which result from processing flue gas from a coal-fired utility boiler.

In conjunction with the pilot plant test program, EPA contracted Radian Corporation to prepare an independent evaluation of the processes tested based on the pilot plant results. This section summarizes the results of the independent evaluation of the HZ process. It includes a discussion of the results of tests conducted by both Chemico and Radian and the results of Radian's independent evaluation of the HZ process. A separate report covering the detailed results of the pilot plant test program has been prepared by HZ.

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## 1.2 PROGRAM OBJECTIVES AND APPROACH

The independent evaluation of the HZ pilot plant test program conducted by Radian Corporation had three major objectives. The first was to provide independent validation of the process measurements made by Chemico. The second objective was to quantify any changes in the emission rates of secondary pollutants (pollutants other than $NO_x$) across the pilot plant reactor. And the third objective was to complete a technical and economic evaluation of the HZ process including identification of areas which require further development or investigation.

In order to validate the measurements made by Chemico, a quality assurance program was implemented. This program used EPA reference methods and other standard measurement techniques to make independent audits of critical process parameters such as flue gas flowrate, $NH_3$ injection rate, etc. In conjunction with the quality assurance program, the continuous $NO_x$ monitors were subjected to certification tests designed to determine the monitors' ability to make accurate, repeatable measurements. These certification tests included measurement of the continuous monitors relative accuracy, drift, calibration error, and response time.

Concurrent with the quality assurance program, a stack sampling program was conducted to measure changes in secondary process emissions across the SCR reactor. This approach required simultaneous sampling of the reactor inlet and outlet for the species of interest. The samples were then analyzed and differences between inlet and outlet concentrations determined.

Based on the results of the quality assurance program, the stack sampling program, and the test data collected by Chemico, an evaluation of the HZ process was completed. This evaluation consisted of several steps. First, the test data were analyzed and reduced to a form which could be used to predict process performance for a specified set of operating conditions. Then, using the reduced test data and the results of the stack sampling program, material and energy balance calculations were completed for a 500 MWe coal-fired application

of the HZ process. The basis for these calculations was identical to that used by TVA in developing cost estimates for the HZ process and presented in "Preliminary Economic Analysis of $NO_x$ The Gas Treatment Processes".[1] The results of the material and energy balance calculations were then used to develop a modified estimate of total capital investment and annual revenue requirements for a 500 MW coal-fired application of the HZ process. Finally, the test data were reviewed and areas requiring further investigation/quantification were identified.

## 1.3 RESULTS

Several areas which influence the technical and economic feasibility of the HZ process were examined as part of this study including:

- the pilot plant test results,

- the results of Radian's independent tests,

- the results of a 500 MW conceptual design of the HZ process,

- the material balance calculations for a 500 MW process application,

- the energy balance calculations for a 500 MW process application, and

- the estimated capital investment and annual revenue requirements for a 500 MW HZ process application.

The following discussion summarizes the results of the evaluation of each of these areas while Section 1.4 presents overall conclusions on the technical and economic feasibility of applying the HZ process to a coal-fired boiler.

## 1.3.1  Pilot Plant Test Results

The test program at the HZ pilot plant was initiated in June 1979, and was completed in January 1981. During this period, the pilot plant processed a flue gas slip stream from between the economizer and the air preheater of the coal-fired unit No. 3 at Georgia Power Company's Plant Mitchell Station. Design flue gas flowrate to the pilot unit was 1700 $Nm^3$/hr (1060 scfm) and flue gas was processed for a total of about 10,000 hours during the program.

The pilot plant test program involved examination of three charges of catalyst material under a variety of test conditions. In general, these tests were divided into two categories:  optimization tests and demonstration or long-term tests. The objective of the optimization tests was to identify operating conditions which would reduce $NO_x$ emissions by 90 percent at a minimum total cost for operating the process. The major objective of the demonstration tests was to document the ability of the process to achieve a 90 percent reduction in $NO_x$ emissions for 90 days.

The objectives of the pilot plant tests conducted by Chemico were met and exceeded. The $NO_x$ reduction efficiency of the plant averaged over 90 percent during the 90 day demonstration test and the average was 89.8 percent over a 5-month period of operation. This included several test periods during which the $NH_3/NO_x$ ratio was varied to determine its effect on $NO_x$ reduction efficiency. If these test periods are excluded from the averages, the $NO_x$ reduction efficiency during the 5-months of operation would be greater than 90 percent.

Some other significant results of the test program showed that neither temperature nor flowrate has as significant effect on $NO_x$ reduction efficiency within a range about the design level. These results indicate that process performance should not be impaired at boiler loads below the design level. As a result, no temperature or flow control would be required for a full-scale application of the HZ process.

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During the test program, 3 charges of catalyst were examined and two of these (NOXNON 500) experienced severe plugging problems after about 2000 hours of operation. When replaced with the NOXNON 600 catalyst, which has larger gas passages, no further plugging problems were observed. The original plugging was believed to be due to the adhesiveness of the fly ash. At high temperatures fly ash samples collected from the power plant were found to agglomerate.

Tests with the NOXNON 500 catalyst did not last long enough to get a good measure of catalyst activity, but results of the NOXNON 600 tests showed a gradual decline in catalyst activity with time. After 5500 hours of operation, activity of the NOXNON 600 had dropped slightly, but it was still possible to achieve 90 percent $NO_x$ reduction. Since 5500 hours is close to one year of operation ($\sim$7000 hours) a catalyst life of 1 year seems reasonable based on the test results. In fact, catalyst life may be extended well beyond 1 year based on the results of the in situ regeneration test conducted at the conclusion of the test program. These tests showed the catalyst activity had been restored to the activity of essentially new catalyst. Unfortunately, since the regeneration test was conducted during the final week of the test program, it is uncertain how long the effects of regeneration would last.

Overall, the results of the pilot plant tests indicate application of the HZ process to a coal-fired boiler is technically feasible. The tests demonstrated the ability of the process to achieve 90 percent $NO_x$ reduction for over 90 days and also demonstrated a stable catalyst life of nearly one year.

1.3.2  Independent Evaluation Test Program Results

The independent evaluation test program conducted by Radian had two primary objectives: to insure the quality of the data collected at the HZ pilot plant and to quantify changes in the concentrations of certain pollutants across the HZ reactor. Data quality was determined by quality assurance (QA) audits and continuous monitor certification tests, while changes in pollutant

concentrations were determined by a secondary emissions sampling program. The results of each of these elements of the independent evaluation program are summarized below.

### Quality Assurance Audits

The QA audits conducted by Radian were designed to insure that the process data which are required to characterize the operation of the HZ pilot plant were accurate. Radian employed reference methods for auditing process operating parameters which were measured on a continuous or routine basis by Chemico. One exception to this was the measurement of $NH_3$ emissions which were not routinely monitored by Chemico, although the original design of the pilot unit included an analyzer intended to determine $NH_3$ emissions.

The results of the $NH_3$ emissions sampling conducted by Radian indicated an average $NH_3$ concentration at the reactor outlet of about 50 ppm under operating conditions which result in 90 percent $NO_x$ reduction. The $NH_3$ concentration at the reactor outlet was much higher than expected (previous work in Japan indicated $NH_3$ concentrations of about 10 ppm). The relatively high $NH_3$ concentrations are expected to have an impact on equipment located downstream of the catalytic reactor for a commercial application of the HZ process. This is discussed in more detail later in this section.

The results of the QA audits conducted by Radian are summarized in Table 1-1. As shown, all but the $SO_2$ concentration measurements were within 10 percent of the values recorded by Chemico. This indicates that with the exception of the $SO_2$ monitor, the process data collected by Chemico accurately characterize the operation of the HZ pilot plant.

TABLE 1-1. RESULTS OF QA AUDITS AT THE
HITACHI ZOSEN PILOT PLANT

| Measurement Audited | Relative Error[1] (%) |
|---|---|
| $SO_2$ Concentration | -19.8 |
| Flue Gas Flowrate | - 0.3 |
| $NH_3$ Injection Rate | - 6.0 |
| Reactor Pressure Drop | 4.5 |
| Reactor Temperature | 4.8 |

[1]Relative Error = $\dfrac{\text{Monitor Reading - Audit Measurement}}{\text{Audit Measurement}}$ x 100%

In the case of the flue gas $SO_2$ concentration at the HZ pilot plant, the audit results were determined to be correct and the $SO_2$ monitor was in error. This error is characteristic of the type of $SO_2$ monitor used (pulsed fluorescence) when the instrument is calibrated with standard gases composed of $SO_2$ in nitrogen.

## Secondary Emissions Sampling

The secondary emissions sampling program was conducted by Radian during July and August 1980, concurrent with the demonstration test conducted by Chemico. The objective was to quantify changes in the emission rates of pollutants other than $NO_x$. For the most part, these tests were conducted during tests in which steady state $NO_x$ reduction efficiency was maintained at 90 percent.

Table 1-2 summarizes the results of the secondary emissions sampling program at the HZ pilot plant. As shown, concentrations of hydrocarbons, carbon monoxide, hydrogen cyanide (HCN), and nitrosoamines at the reactor outlet were below the detection limit of the analytical techniques employed. For hydrocarbons and carbon monoxide no conclusions can be drawn concerning the impacts of the HZ process on these pollutants. For HCN, the analytical detection limit is equivalent to 10 ppbv and for N-Nitrosodimethylamine, 2 ppbv. In both cases, these concentrations are at levels which are considered safe for emission sources.

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Table 1-2 does show an increase in $SO_3$ concentration across the HZ reactor. This is due to oxidation of $SO_2$ in the reactor and was not unexpected since the catalyst contains vanadium pentoxide which is the catalyst used in manufacture of sulfuric acid. The apparent change in particulate concentration shown in Table 1-2 is believed to be due to unaccounted for stratification in the ducts. It should be noted that no results for nitrous oxide ($N_2O$) are presented. This is due to the fact that the analytical technique used to measure $N_2O$ proved unsatisfactory for use in a flue gas stream.

TABLE 1-2. STACK SAMPLING RESULTS AT HZ PILOT UNIT

| Flue Gas Component | Reactor Inlet Concentration[1] | Reactor Outlet Concentration[1] |
|---|---|---|
| Nitrosoamines[2] ($\mu g/dscm^2$) | 5 | 5 |
| Hydrogen Cyanide (mg/dscm) | .01 | .01 |
| Ammonia (ppmv-dry basis) | Not measured | 54.8 |
| Sulfur Trioxide (ppmv-dry basis) | 8.4 | 20.7 |
| Hydrocarbons[3] ($C_1$-$C_6$) (ppmv) | 1.0 | 1.0 |
| Carbon Monoxide[3] (%) | 0.017 | 0.017 |
| Particulate Loading (gm/dscm) | 7.1 | 7.7 |
| Nitrous Oxide | - | - |

[1]Average of 3 or more tests
[2]dscm – dry standard cubic meter
[3]Below the detection limit

In addition to measuring the concentration of particulates in the flue gas, an elemental analysis of the particulates was completed in an attempt to determine if erosion of the catalyst has a measurable effect on the

concentration of Vanadium (V) and Titanium (Ti) in the particulates.
Table 1-3 presents the results of the elemental analysis of the particulates
collected at the HZ pilot plant. As shown, an apparent increase in all
elements occurs across the reactor, but the relative concentrations on V
and Ti remain constant. This indicates that there is no measurable change
in the concentration of V or Ti in the particulates exiting the reactor.

TABLE 1-3. RESULTS OF PARTICULATE ANALYSIS AT THE HZ PILOT PLANT[1]

| Component | In | Out | Out/In |
|---|---|---|---|
| Al | 10.7% | 13.0% | 1.21 |
| Ca | 8200 ppm | 9900 ppm | 1.21 |
| Fe | 4.9% | 6.0% | 1.22 |
| K | 2.0% | 2.5% | 1.25 |
| Mg | 6300 ppm | 7800 ppm | 1.24 |
| Mn | 190 ppm | 240 ppm | 1.26 |
| Sn | 490 ppm | 680 ppm | 1.40 |
| Na | 4200 ppm | 4700 ppm | 1.12 |
| Si | 18% | 23% | 1.28 |
| Zn | 190 ppm | 250 ppm | 1.32 |
| Cu | 150 ppm | 170 ppm | 1.13 |
| Ti | 5800 ppm | 6900 ppm | 1.19 |
| V | 270 ppm | 330 ppm | 1.22 |

[1]Concentrations are on a mass fraction basis

Continuous Monitor Certification Tests

Certification tests were conducted for the $SO_2$ and $NO_x$ monitors used to
measure flue gas concentrations of pollutants at the inlet and outlet of the
reactor. These tests were included in the independent evaluation program to
insure the quality of the pilot plant performance data being collected by
Chemico. Certification of continuous emission monitors involves a formal
procedure which has been developed by EPA to insure the accuracy of monitors

measuring emissions from sources which must comply with new source performance standard emission limitations. In order for a continuous emission monitor (CEM) to be certified, it must be subjected to and pass a number of performance tests, including:

- calibration error,

- response time,

- drift, and

- relative accuracy.

The performance specifications for each of the above certification tests are presented in Table 1-4 along with the results of the certification tests. The performance specifications are those contained in the Federal Register, Vol. 44, No. 197, Wednesday, October 10, 1979 - "Proposed Rules: Standards of Performance for New Stationary Sources; Continuous Monitoring Performance Specifications".[2]

TABLE 1-4. CONTINUOUS MONITOR CERTIFICATION TEST
RESULTS AT THE HZ PILOT PLANT

| Certification Test | Performance Specification | Inlet $NO_x$ Monitor | Outlet $NO_x$ Monitor |
|---|---|---|---|
| Calibration Error | | | |
| –high level (%) | ≤5 | 1.40 | 4.70 |
| –mid level (%) | ≤5 | 4.39 | 2.68 |
| Response Time (min) | ≤15 | 1.4 | 1.6 |
| Zero drift (2-hour) (%) | ≤2 | 1.20 | 0.05 |
| Calibration Drift (%) (2-hour) | ≤2 | 1.93 | 1.78 |
| Relative Accuracy (%) | ≤20[1] | 14.1 | 10.5 |

[1]Alternatively, <10 percent of the applicable emissions standard.

As shown in Table 1-5, the test results for both the $NO_x$ continuous monitors met the performance specifications. These data indicate that continuous monitors were making accurate measurements of flue gas $NO_x$ concentrations.

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## 1.3.3 Results of the Conceptual Design of a 500 MW HZ Process

A conceptual design of a 500 MW HZ process was prepared based on the pilot plant test results. This conceptual design served as a basis for material and energy balance calculations and for a cost estimate for a 500 MW application of the HZ process.

Table 1-5 summarizes the results of the conceptual design for a 500 MW application of an HZ process. As shown, the key design variable levels are presented for the SCR reactor and the downstream air preheater.

TABLE 1-5. RESULTS OF THE CONCEPTUAL DESIGN FOR A 500 MW HITACHI ZOSEN PROCESS

| Design Parameter | Design Level |
|---|---|
| **Reactor Design Parameter** | |
| • Number of Reactors | 2 |
| • Reactor Crossection ($m^2$) | 96.5 |
| • Catalyst Volume per reactor ($m^3$) | 205 |
| • Reactor System Pressure Drop (kPa) | 1.28 |
| • Soot Blowers per Reactor | 4 |
| • Soot Blowing Frequency | 3/day |
| **Air Preheater Design Parameters** | |
| • Soot Blowers per Preheater | 6 |
| • Soot Blowing Frequency | 6/day |
| • Element Configuration | Combined Intermediate and Low Temperature Zone |
| • Element Construction | Corrosion Resistant Material in Intermediate-Low Temperature Zone |

The conceptual design of the HZ process was prepared for a single application of the process and it was based solely on the pilot plant test results. The results of this design indicate that it is possible to reduce $NO_x$ emissions by 90 percent using the HZ process. In fact, 90 percent $NO_x$ reduction was possible at space velocities greater than previous estimates indicated (i.e., at a relatively lower catalyst volume per unit volume of flue gas treated). However, the greater space velocities were accompanied by $NH_3$ emissions which were much higher than previous estimates.

One result of the high $NH_3$ emissions estimated for the conceptual design was that special modifications to the air preheater are required to mitigate problems associated with the formation of ammonium sulfates downstream of the reactor. These modifications were identified as part of a prior study[3] and they are based on Japanese experience with air preheater operation downstream of an SCR system. It should be noted that the modifications specified for the air preheater were expected to minimize problems at relatively low $NH_3$ and $SO_3$ concentrations at the reactor exit. The concentrations at the reactor outlet for the conceptual design are much higher than anticipated in previous studies of SCR technology and this could result in operational problems which cannot be minimized by the preheater modifications included in the conceptual design. This represents an area which requires durther investigation.

Reactor pressure drop and other design parameters are fairly consistent with previous estimates for the process. The design results also show that the process can operate over a range of temperatures (340 to 410°C) and space velocities (6,500 to 8,900 hr$^{-1}$) without any significant effect on $NO_x$ reduction efficiency. This indicates the process has good flexibility in processing flue gas under conditions of changing boiler load.

In summary, the conceptual design indicates that the HZ process can reduce $NO_x$ emissions by 90 percent. And, this $NO_x$ reduction efficiency can be achieved at a lower catalyst volume per unit of flue gas treated than

previous estimates indicated. However, the lower catalyst volume of the conceptual design is accompanied by a significantly higher $NH_3$ emission rate which can result in severe operational problems in downstream equipment, particularly the air preheater. Further work is required to determine if the effects of these $NH_3$ emissions can be offset by the air preheater modifications included in the conceptual design.

## 1.3.4 Results of the Material Balance Calculations for a 500 MW HZ Process

Material balance calculations for a 500 MW application of the HZ process were included as part of this study to identify raw material requirements for the process and to serve as a basis for an estimate of capital investment and annual revenue requirements. The material balance was based on the pilot plant and secondary emissions sampling test results and thus reflects those results in the estimated raw material requirements. The most significant results of the material balance calculations include estimation of $NH_3$ requirements for $NO_x$ reduction, $NH_3$ and $SO_3$ emissions from the process, and steam requirements for air preheater soot blowing.

The $NH_3$ requirements for the process were estimated to be 1.0 mole of $NH_3$ per mole of $NO_x$ in the flue gas entering the reactor. This requirement was estimated based on the results of approximately 6 months of pilot plant operation. During that 6 month period, the $NH_3/NO_x$ injection ratio averaged 0.98 while the $NO_x$ reduction efficiency averaged 89.8 percent. With the $NH_3/NO_x$ injection ratio of 1.0, estimated $NH_3$ requirements for the process decreased about 10 percent for previous estimates.

Estimates of $NH_3$ and $SO_3$ emissions from the HZ process were significantly higher than previous estimates indicated. As discussed earlier, this results in the requirements for air preheater modifications and additional soot blowing. The requirement for additional soot blowing results in a sevenfold increase in HZ process steam requirements. However, this is not very significant from a material balance standpoint, but it is important in terms of its effect on

process energy requirements. It should be noted that HZ claims the $NH_3$ emission and $SO_2$ oxidation rates can be reduced with no decrease in process performance by adjusting the composition of the catalyst. However, since this was not demonstrated during the pilot plant tests it was not considered in preparing the material balances or the conceptual design.

In summary, the material balance calculations showed no significant change in raw material requirements for the HZ process. The most important result was the estimated $NH_3$ and $SO_3$ emission rates which were significantly higher than previous estimates indicated.

## 1.3.5 Results of the Energy Balance Calculations for a 500 MW HZ Process

An energy balance was completed as part of the evaluation of the HZ process. This energy balance defined overall process energy requirements and quantified the heat credits associated with the process. The results of the analysis of energy requirements indicated that the HZ process has a net energy consumption equivalent to about 0.3 percent of the energy input to the boiler.

The individual components of the overall process energy requirements are summarized in Table 1-6. Each of these components has been put on the basis of heat input to the boiler. For steam, a thermal efficiency of 88 percent was used to determine the energy input required to generate one Gcal of steam energy. For electricity, a boiler heat rate of 2.27 Mcal/kWh was used. The heat credit was assumed to replace heat input to the boiler on a 1-to-1 basis.

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TABLE 1-6.  OVERALL ENERGY REQUIREMENT FOR A 500 MW
APPLICATION OF THE HZ PROCESS

| Energy Area | Energy Requirement (Gcal/hr) | Percent of Boiler Capacity |
|---|---|---|
| Heat Credit | (3.15) | (0.28) |
| Steam | 3.36 | 0.30 |
| Electricity | 3.50 | 0.31 |
| Total | 3.99 | 0.33 |

## 1.3.6 Results of the Cost Estimate for a 500 MW HZ Process Application

An estimate of total capital investment and annual revenue requirements for a 500 MW application of the HZ process was prepared as part of this evaluation. The estimated costs reflect the results of the pilot plant tests. When compared with the previous estimate prepared by TVA, the modified cost estimates indicate the magnitude of the impact the pilot plant results had on estimated process costs. In addition, comparison of the modified cost estimate with cost estimates for other SCR processes is an indicator of the cost effectiveness of the HZ process as tested in the pilot plant program.

### Results of Capital Cost Estimate

Table 1-7 presents the individual components and the estimated total capital investment for a 500 MW application of the HZ process. As shown, the total capital investment was estimated to be approximately $22.1 x $10^6$ which is equivalent to approximately $44/kW of generating capacity. When compared to TVA's previous estimate, this represents a slight decrease in total capital investment. The principal difference between the two estimates is the estimated catalyst volume. The required catalyst volume based on the pilot plant tests was estimated to be about 20 percent less, thereby decreasing the total capital investment. However, the decrease in costs from reduced catalyst volume requirements was somewhat offset by the costs of air preheater modifications required to minimize ammonium sulfate deposition problems.

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TABLE 1-7. ESTIMATED CAPITAL INVESTMENT FOR A 500 MW APPLICATION OF THE HITACHI ZOSEN PROCESS[a]

| | Investment, $ | % of total direct investment |
|---|---|---|
| Direct Investment[b] | | |
| NH₃ storage and injection | 645,000 | 5.5 |
| Reactor section | 8,632,000 | 73.4 |
| Gas handling | 351,000 | 3.0 |
| Air preheater modifications | 1,461,000 | 12.4 |
| Sub-total direct investment (DI) | 11,089,000 | 94.3 |
| Services, utilities (0.06 x DI) | 665,000 | 5.7 |
| Total direct investment (TDI) | 11,754,000 | 100.00 |
| | | |
| Indirect Investment | | |
| Engineering design and supervision | 274,000 | 2.3 |
| Architect and engineering contractor | 69,000 | 0.6 |
| Construction expense = $0.25 \, (TDI \times 10^{-6})^{0.83}$ | 1,933,000 | 16.4 |
| Contractor fees = $0.096 \, (TDI \times 10^{-6})^{0.76}$ | 625,000 | 5.3 |
| Total indirect investment (IDI) | 2,901,000 | 24.7 |
| Contingency = 0.2 (TDI + IDI) | 2,931,000 | 24.9 |
| Total fixed investment (TFI) | 17,586,000 | 149.6 |
| | | |
| Other Capital Charges | | |
| Allowance for startup and modifications = (0.1) (TFI) | 1,759,000 | 15.0 |
| Interest during construction = (0.12) (TFI) | 2,110,000 | 17.9 |
| Total depreciable investment | 21,455,000 | 182.5 |
| Land | 5,000 | - |
| Working capital | 336,000 | 2 9 |
| Royalty fee | 300,000 | 2.6 |
| TOTAL CAPITAL INVESTMENT | 22,096,000 | 188.0 |

[a]Basis: 500 MW new coal-fired power plant, 3.5% sulfur coal, 90% NOₓ removal. Midwest plant location. Represents project beginning mid-1977, ending mid-1980. Average basis for scaling, mid-1979. Investment requirements for fly ash disposal excluded. Construction labor shortages with overtime pay incentive not considered.

[b]Each item of direct investment includes total equipment costs plus installation labor, and material costs for electrical, piping, ductwork, foundations, structural, instrumentation, insulation, and site preparation.

## Results of the Annual Revenue Requirement Estimate

Table 1-8 presents the individual components and the total estimated average annual revenue requirements for a 500 MW application of the HZ process. As shown, the average annual revenue requirement was estimated to be approximately $10.2 x $12^6$ which is equivalent to 2.91 mills/kWh. When compared to TVA's previous estimate this represents a 17 percent decrease in the annual revenue requirements for the process.

As with the capital costs, the principal factor which decreased the annual revenue requirements is the lower quantity of catalyst required in the reactor. Again, this reduction in annual revenue requirements was somewhat offset by the costs of increased air preheater soot blowing.

## Cost Comparison and Summary

The capital investment and annual revenue requirements of the HZ process have been estimated based on the results of the test conducted at the EPA sponsored pilot plant in Albany, Georgia. The results of these cost estimates indicate that the capital costs and annual revenue requirements are slightly lower than the estimated costs prior to the test program. A more important comparison, however, is the cost of the HZ process relative to the cost of other SCR processes.

Since the same basis was used in preparing the modified HZ cost estimate as TVA used in preparing preliminary economic estimates for other SCR processes, it is possible to make a direct comparison with the costs of the Shell Flue Gas treating (SFGT) Process which were developed under the EPA pilot plant test program. Table 1-9 presents the estimated annual revenue requirements for two pollution control systems which reduce emissions of particulates, $NO_x$, and $SO_3$ by 99.5, 90, and 90 percent, respectively. As shown, the pollution control systems include flue gas desulfurization capability and have ESP's located downstream in order to put the cost estimates on a common basis.

TABLE 1-8.  ESTIMATED AVERAGE ANNUAL REVENUE REQUIREMENTS FOR A 500 MW APPLICATION OF THE HITACHI ZOSEN PROCESS[a]

| Item | Annual quantity | Unit cost($) | Annual cost($) | % of annual revenue required |
|---|---|---|---|---|
| **Direct Costs** | | | | |
| Raw materials | | | | |
| NH$_3$ | 5.25 x 10$^6$ kg | 0.165/kg | 866,300 | 8.47 |
| Catalyst | | | 5,125,000 | 50.14 |
| Total raw materials | | | 5,991,300 | 58.61 |
| Conversion costs | | | | |
| Operating labor and supervision | 8760 labor hrs. | 12.50/ labor hr. | 109,500 | 1 07 |
| Utilities | | | | |
| Steam | 20,700 Gcal | 7.94/Gcal | 164,400 | 1.61 |
| Electricity | 10,787,000 kWh | 0.029/kWh | 312,800 | 3.06 |
| Heat credit | 22,050 Gcal | -7.94/Gcal | (175,100) | (1.71) |
| Maintenance = .04 x TDI | | | 470,200 | 4.60 |
| Analyses | 2,920 labor hrs. | 17.00/ labor hr. | 49,600 | 0 48 |
| Total conversion costs | | | 931,400 | 9.11 |
| Total direct costs | | | 6,922,700 | 67.72 |
| **Indirect Costs** | | | | |
| Capital charges | | | | |
| Depreciation = (0.06) (total depreciable investment) | | | 1,287,300 | 12.59 |
| Average cost of capital = (0.086) x (total capital investment) | | | 1,900,300 | 18 59 |
| Overheads | | | | |
| Plant = (0.5) (conversion costs minus utilities) | | | 314,700 | 3.08 |
| Administrative = (0.1) (operating labor costs) | | | 11,000 | 0.11 |
| Total indirect costs | | | 3,513,300 | 34.37 |
| Spent catalyst disposal | | | (214,000) | (2.09) |
| TOTAL ANNUAL REVENUE REQUIREMENTS | | | 10,222,000 | 100 00 |

[a]Basis:  500 MW new coal-fired power plant, 3.5% S coal. 90 percent NO$_x$ reduction, 90 percent SO$_2$ removal. Midwest power plant location, 1980 revenue requirements.  Remaining life of power plant = 30 years.  Plant on line 7000 hr/yr.  Plant heat rate equals 9.5 MJ/kWh.  Investment and revenue requirement for disposal of fly ash excluded.  Total direct investment $11,754,000; total depreciable investment $21,455,000; and total capital investment $22,096.000.

TABLE 1-9.  ESTIMATED ANNUAL REVENUE REQUIREMENTS FOR TWO
POLLUTION CONTROL SYSTEMS[1]

| SCR Process | Annual Revenue Requirements ($ x $10^{-6}$) | | | |
| | SCR | FGD | ESP | Overall |
| --- | --- | --- | --- | --- |
| SFGT | 33.6 | – | 3.0 | 36.6 |
| Hitachi Zosen | 10.2 | 14.7 | 2.2 | 27.1 |

[1]All costs except the HZ-SCR and the SFGT-SCR costs are from "Preliminary
Economic Analysis of $NO_x$ Flue Gas Treatment Processes." Tennessee Valley
Authority - Office of Power.  EPA-600/7-80-021, February, 1980.

As shown in Table 1-9, the estimated costs associated with the HZ
processes are 30 percent lower than those of the SFGT process.  These results
indicate that the HZ process, as tested in the pilot plant and presented in
the conceptual design, the most economical of the two SCR processes tested
in EPA's pilot plant program within the constraints of the conceptual design
used in this study.  It should be noted that the relative costs presented in
Table 1-9 are only valid for one specific application and they could change
for other applications.

Overall the results of the modified cost estimate indicate that, for the
particular application examined in this study, the HZ process is economically
competitive with other SCR processes.  This is based on a conceptual design
which was representative of operating conditions demonstrated during the
pilot plant tests.  It should be noted, however, that the costs can be
affected by the impacts of high $NH_3$ and $SO_3$ emissions whose effects were not
examined during the pilot plant tests.  Additionally, the estimates presented
in this evaluation were based on a 1-year catalyst life which was not demon-
strated.  But, HZ will guarantee a 1-year catalyst life for coal-fired appli-
cations.

## 1.4 CONCLUSIONS

The following discussion presents conclusions based on the work performed during this study. For the most part, the information obtained during the course of the study is summarized in this report and serves as background for the conclusions presented here. The major conclusions of this study are:

- The HZ process can reduce $NO_x$ emissions by 90 percent when applied to a coal-fired boiler. This level of emissions reduction was achieved over a 90-day period at an $NH_3/NO_x$ injection ratio of 1.0 and space velocities greater than previous test work indicated. However, the excellent performance of this pilot plant was accompanied by $NH_3$ emissions which were much higher than previous estimates indicated.

- The initial tests of the HZ process experienced problems with catalyst plugging which resulted in failure of 2 charges of NOXNON 500 series catalyst. These problems were eliminated by employing NOXNON 600 series catalyst (a catalyst with larger gas passages) and the use of compressed air (as opposed to superheated steam) for reactor soot blowing. It appears likely that the good performance of the NOXNON 600 catalyst was due to the larger gas passages since the fly ash has a tendency to agglomerate in dry environments.

- A gradual decline in catalyst activity was recorded over the duration of the test program which resulted in the requirement for increased $NH_3/NO_x$ injection ratios to attain 90 percent $NO_x$ reduction. Because the test program was terminated after 5500 hours of operation, the catalyst activity after 1 year of operation could not be determined.

- A novel, in situ catalyst regeneration technique was tested as part of the program. This test showed that the regenerated catalyst had activity similar to fresh catalyst and thus reversed some of the decline in activity observed over the duration of the test program. Unfortunately, the catalyst regeneration technique was tested toward the end of the pilot plant test program and so it is uncertain how long the effects of the catalyst regeneration will last.

- The independent evaluation test program indicated that emission rates of most pollutants were not affected by the HZ process. However, emission rates of both $NH_3$ and $SO_3$ were relatively high and those emissions can result in operational problems in downstream equipment. The severity of any problems in this regard are very site specific and could not be assessed as part of this study. This should, however, be given careful consideration in any planned applications of the HZ process.

- The conceptual design and material balance calculations indicated high $NH_3$ emission rates which will cause severe operational problems in the air preheater located downstream of the HZ process. The conceptual design included air preheater modifications designed to minimize those problems. But because the estimated $NH_3$ and $SO_3$ emission rates are much higher than previous estimates, it is uncertain if the air preheater modifications will prove adequate. Further investigation in this area is required.

- The overall energy requirements for the HZ process were estimated to be 0.3 percent of the boiler's capacity. This is a very small fraction of boiler capacity and it does not significantly affect process costs.

- The estimated capital investment and annual revenue requirements for the HZ process were slightly lower than TVA's preliminary estimate. This indicates that the HZ process is economically competitive with other SCR processes when considered for application to a coal-fired boiler. It should be noted that the cost estimates assumed a 1-year catalyst life which was not quite demonstrated during the pilot plant tests although it would be guaranteed by HZ. The relative process costs could change if a 1-year catalyst life is not possible.

In conclusion, the pilot plant test results indicate the HZ process is technically suited for application to coal-fired sources. However, the tests did not demonstrate a 1-year catalyst life which is generally considered a minimum for technical feasibility of an SCR process. In reality, a shorter catalyst life would translate into increased annual revenue requirements. In terms of costs, under the conditions of the cost estimate prepared as part of this study, the HZ process is economically competitive with other SCR processes.

# SECTION 2

## INTRODUCTION

Selective catalytic reduction (SCR) processes have been shown to be the most effective method for high levels of nitrogen oxide ($NO_x$) control for stationary sources. Numerous SCR units have been installed on both oil- and gas-fired utility boilers, industrial boilers, and process heaters and furnaces in Japan. Many of these units continuously achieve $NO_x$ reductions of >80% giving SCR the highest $NO_x$ reduction of any system available commercially.

SCR systems utilize ammonia ($NH_3$) to reduce $NO_x$ to molecular nitrogen and water on the surface of a catalyst. The overall $NO_x$ reduction reactions are summarized in Equations 2-1 and 2-2.

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O \qquad (2-1)$$

$$2NO_2 + 4NH_3 + O_2 \rightarrow 3N_2 + 6H_2O \qquad (2-2)$$
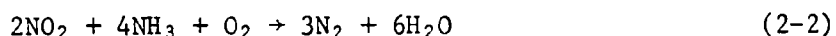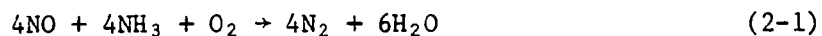
The commercially available SCR catalysts perform optimally at temperatures of 300-400°C (570-750°F). For utility boiler applications, flue gas is at these temperatures downstream of the economizer and upstream of the air preheater. With industrial boilers these temperatures may exist upstream of the economizer.

SCR processes were originally developed in Japan and have been applied primarily to oil- and gas-fired units. SCR systems are being installed in the U.S. on a limited basis. Several oil-fired process heaters and one utility boiler in California have been equipped with SCR systems. The latter

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is under construction at Southern California Edison's Huntington Beach plant. This SCR system will treat half of the flue gas from a 215 MWe oil-fired utility boiler.

In Japan (and in the U.S.) current efforts are directed towards developing SCR systems for coal-fired applications. Presently, there are two commercial SCR systems treating flue gas from coal-fired boilers with more systems due to come on line later this year.

The transfer of SCR technology from Japan to the U.S. for coal-fired applications presents a potentially significant problem. Since most coal-fired boilers in the U.S. operate ESP's located downstream of the air pre-heater, the catalyst in an SCR reactor would be exposed to the full particulate concentration from the boiler. And although tests have been conducted in Japan in which the catalyst was exposed to high particulate concentrations with no adverse effects, the differences in the composition of particulates from U.S. and Japanese coals could impact SCR operation.

In an effort to further the development of SCR technology and in particular to determine how differences between Japanese and U.S. coal/particulate properties impact the performance of SCR processes, EPA has sponsored pilot scale tests of two SCR systems. The SCR systems tested were the Hitachi Zosen (HZ) process and the Shell flue gas treating (SFGT) process, which is also capable of removing $SO_2$ from the flue gas. In both cases, the pilot plants processed a flue gas slipstream from a coal-fired boiler. The contractors responsible for the design and operation of these pilot plants were Chemico Air Pollution Control Corporation (now General Electric Environmental Services Corporation), which is the North America licensee for the HZ process, and the Process Division of UOP, who is the licensing agency for the SFGT process. These contractors were also responsible for collecting, evaluation, and reporting of the test data.

The main objectives of the pilot plants were to demonstrate the capability of continuously achieving 90% $NO_x$ removal (and 90% $SO_2$ removal simultaneously for the SFGT process) and to determine the effects of coal-fired flue gas on long-term catalyst activity. Other objectives of the test program were to determine the optimum operating conditions for the process and the raw material and utility demands. This information is needed to make an accurate evaluation of the design and costs for a commercial scale SCR system.

To perform the evaluation of the two SCR processes EPA contracted Radian Corporation as an independent consultant. This report presents the results of Radian's evaluation of the HZ process. A separate report was prepared for the evaluation of the SFGT process.

Radian Corporation's independent evaluation of the HZ process had three primary objectives. The first was to provide independent validation of the data measurements made by Chemico. Second, Radian was to quantify any change (either production or reduction) in selected secondary pollutants (pollutants other than $NO_x$) across the reactor. Finally, using both Radian and Chemico data, a technical evaluation of the HZ process was to be prepared including the identification of areas which require further development before the process can be commercialized.

To validate the data collected by Chemico, Radian instituted stack sampling and quality assurance programs. The relative accuracy of the continuous NOx monitors were determined by stack sampling using EPA reference Method 7. The NOx monitors were also tested for calibration error, response time, and two-hour zero and calibration drift. The results for each of these tests were checked against the minimum performance required by the New Source Performance Standard (NSPS) presently in effect for continuous monitors on utility boilers. If the monitors failed the test, the cause was determined and the test was repeated. The quality assurance program also utilized standard procedures for measuring important operating variables such as $NH_3$ injection flow rate, flue gas flow rate, reactor pressure drop, reactor temperature, etc.

Along with the data validation efforts, Radian conducted a stack sampling program to quantify the amounts of various secondary pollutants entering and exiting the reactor. Samples from the reactor inlet and outlet were collected simultaneously. These samples were then analyzed to determine any change in concentration across the reactor.

Using the results of Radian's stack sampling and quality assurance programs and Chemico's process data, a technical evaluation of the HZ process was performed. The data were reduced and used to determine the operating conditions necessary to obtain 90% $NO_x$ removal. Using these operating conditions and the stack sampling results, material and energy balances for the HZ system were prepared for a 500 MWe coal-fired utility boiler application. The bases used in these calculations were the same as those used by TVA in their "Preliminary Economic Analysis of $NO_x$ Flue Gas Treatment Processes".[1] The calculations were compared to TVA's and incremental costs were estimated. Areas requiring further development were then identified.

This report describes the evaluation of the HZ process pilot plant by Radian Corporation. Section 3 characterizes the field test program including the descriptions of the pilot plant and the test programs of Chemico and Radian. Section 4 contains the results of field tests conducted by both Chemico and Radian measurements. Section 5 presents the technical evaluation of the HZ process including process performance variables, raw material and utility requirements, and downstream impacts. Finally, Section 6 lists the process development requirements.

# SECTION 3

## FIELD TEST PROGRAM

To demonstrate the application of SCR processes on coal-fired boilers, EPA contracted Hitachi-Zosen (HZ) to construct and operate an SCR pilot plant in May 1978. Implementing the contract, HZ provided the basic design of the pilot plant and the proprietary SCR catalyst. Chemico Air Pollution Control Corporation, the major subcontractor, was responsible for the detailed design and engineering, construction, and operation of the pilot plant. This pilot plant was designed to demonstrate the capability of the HZ process to reduce $NO_x$ emissions from a coal-fired boiler in the U.S. by 90 percent.

HZ completed the basic process design in Japan in June 1978. In September 1978 Chemico completed Phase I activities including the detailed plant design and equipment specifications. Phase II - the procurement of equipment, construction subcontractor selection, and pilot plant construction and erection - was finished by July 1979. Chemico then started up the pilot plant and began debugging operations in preparation for the Phase III optimization tests. This work covered the period from July 1979 to May 1980. (The length Phase III was due to the use of three different catalyst charges. This is explained in more detail in Section 4.) Finally, the long-term demonstration test, Phase IV, was conducted from June 1980 to January 1981 at which time the pilot plant was shut down.

Radian Corporation performed its field test programs during July and August 1980. This report section describes in detail the test programs conducted by Chemico and Radian. To provide background information, a discussion of the HZ process and a description of the pilot plant (including details of flow rates, equipment sizes, process instrumentation, and plant operations) are presented as a prelude to the test program discussions.

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## 3.1 HZ PROCESS

The HZ process is one of a number of dry SCR processes. With the appropriate catalyst, ammonia will selectively reduce $NO_x$, in the presence of oxygen, to nitrogen and water on the catalyst surface. The homogeneous, gas-phase reactions are summarized in Equations 3-1 and 3-2.

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O \qquad (3-1)$$

$$2NO_2 + 4NH_3 + O_2 \rightarrow 3N_2 + 6H_2O \qquad (3-2)$$
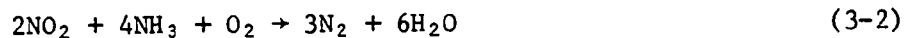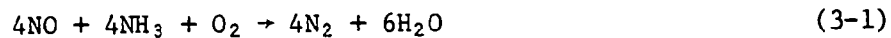
For coal-fired flue gas applications and other gases containing large amounts of sulfur oxides ($SO_x$), the HZ process uses a catalyst composed of titanium dioxide ($TiO_2$) and vanadium pentoxide ($V_2O_5$). This catalyst formulation is resistant to "poisoning" by $SO_x$ and possesses an optimum reaction temperature range of 350-400°C. At temperatures above this range, an additional reaction that becomes increasingly more significant is the oxidation of $NH_3$ to $NO_x$ shown in Equation 3-3. High temperatures can also sinter the catalyst thereby permanently reducing its activity.

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O \qquad (3-3)$$

At temperatures below this range, the kinetics of the $NO_x$ reduction reactions decrease, thus lowering the $NO_x$ reduction efficiency of the system. Another negative impact of lower temperatures is the formation and deposition of ammonium sulfates by the reaction of $NH_3$ with sulfur trioxide ($SO_3$) present in the flue gas (Equations 3-4 and 3-5).

$$NH_3(g) + SO_3(g) + H_2O(g) \rightarrow NH_4HSO_4(1,s) \qquad (3-4)$$

$$2NH_3(g) + SO_3(g) + H_2O(g) \rightarrow (NH_4)_2SO_4(s) \qquad (3-5)$$
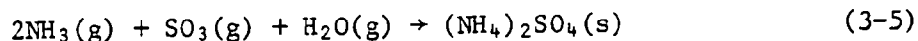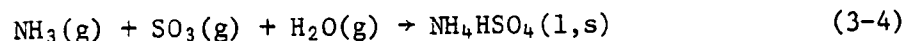
These formation reactions become especially important in downstream heat recovery equipment where the flue gas is cooled.

The formation of ammonium sulfates downstream will be enhanced by the $SO_2$ oxidation capability of the SCR catalyst shown in Equation 3-6. One of the primary components of the SCR catalyst, $V_2O_5$, is the catalyst used commercially to oxidize $SO_2$ in sulfuric acid plants.

$$SO_2(g) + \tfrac{1}{2}O_2(g) \rightarrow SO_3(g) \qquad (3-6)$$

Approximately 1 to 2 percent of the inlet (to the reactor) $SO_2$ is oxidized to $SO_3$ by the SCR catalyst. This will be discussed further in Sections 4 and 5.

To design an SCR system, one must consider the specific characteristics of the flue gas stream, particularly regarding fly ash loadings. For coal-fired applications and other particulate-laden gases, a special physical design of the catalyst was developed by HZ to resist plugging by particulate matter. The catalyst is made up of steel plates that are chemically and thermally treated to allow coating of catalyst on the surface. Then the plates are arranged in a "honeycomb" shape and assembled into units called "cells". The cells (the number of which depends on the size of the gas stream being treated) are then stacked inside the reactor. The flue gas flows through the open channels parallel to the surface of the catalyst-coated plates. The fly ash can pass through the open channels without plugging the catalyst bed. The flue gas components involved in $NO_x$ reduction reactions diffuse (by molecular diffusion for low flows and by eddy diffusion for more turbulent flows) to the catalyst surface where the reactions occur.

3.2  HITACHI-ZOSEN PILOT PLANT DESCRIPTION

The HZ pilot plant was located in Albany, Georgia at the Plant Mitchell station of the Georgia Power Company. Flue gas for the pilot plant was obtained from the Unit No. 3 duct after the boiler economizer but upstream of the air preheater. The flue gas slipstream was first passed through an electric heater to provide temperature control and to compensate for heat losses in the duct from the boiler to the pilot unit. Then ammonia was injected into the gas and the gas was passed down through the catalyst bed. The gas was then

passed through a mechnical collector (cyclone) for particulate removal, an induced draft fan, and then returned to the boiler duct. Figure 3-1 shows a schematic of the HZ pilot plant.

The average flue gas flow rate of the pilot plant was 2210 $Nm^3/hr$ (1370 scfm) which is approximately equal to the flue gas flow from 0.7 MW of electrical power generation. The concentrations of the primary flue gas constituents entering the pilot plant are listed in Table 3-1. (As discussed previously, the fly ash loading shown in Table 3-1 represents the full loading from the boiler.)

TABLE 3-1. APPROXIMATE AVERAGE COMPOSITION OF FLUE GAS
AT HZ/CHEMICO PILOT PLANT INLET

| Constituent | Concentration |
|---|---|
| $N_2$ | 69% by volume |
| $CO_2$ | 18% by volume |
| $H_2O$ | 8% by volume |
| $O_2$ | 5% by volume |
| $SO_2$ | 890 ppmv |
| $NO_x$ | 450 ppmv |
| Particulates | 7.1 gm/dscm (3.1 gr/dscf) |

The operating parameters of the pilot plant which are continuously controlled are:

- flue gas flow rate,
- flue gas temperatures, and
- $NH_3$ flow rate (set by the $NH_3:NO_x$ mole ratio controller).

Table 3-2 lists the instruments used by Chemico to monitor the performance of the pilot plant. This list is not a complete list of all the instruments

NH$_3$ Injection

Electric
Flue Gas
Heater

Hitachi
Zosen
Catalytic
Reactor

Flue Gas
Blower

Return to
Main Flue

Inlet
Sample
Point

From Unit 3
Economizer

Outlet
Sample Point

Cyclone
Collector
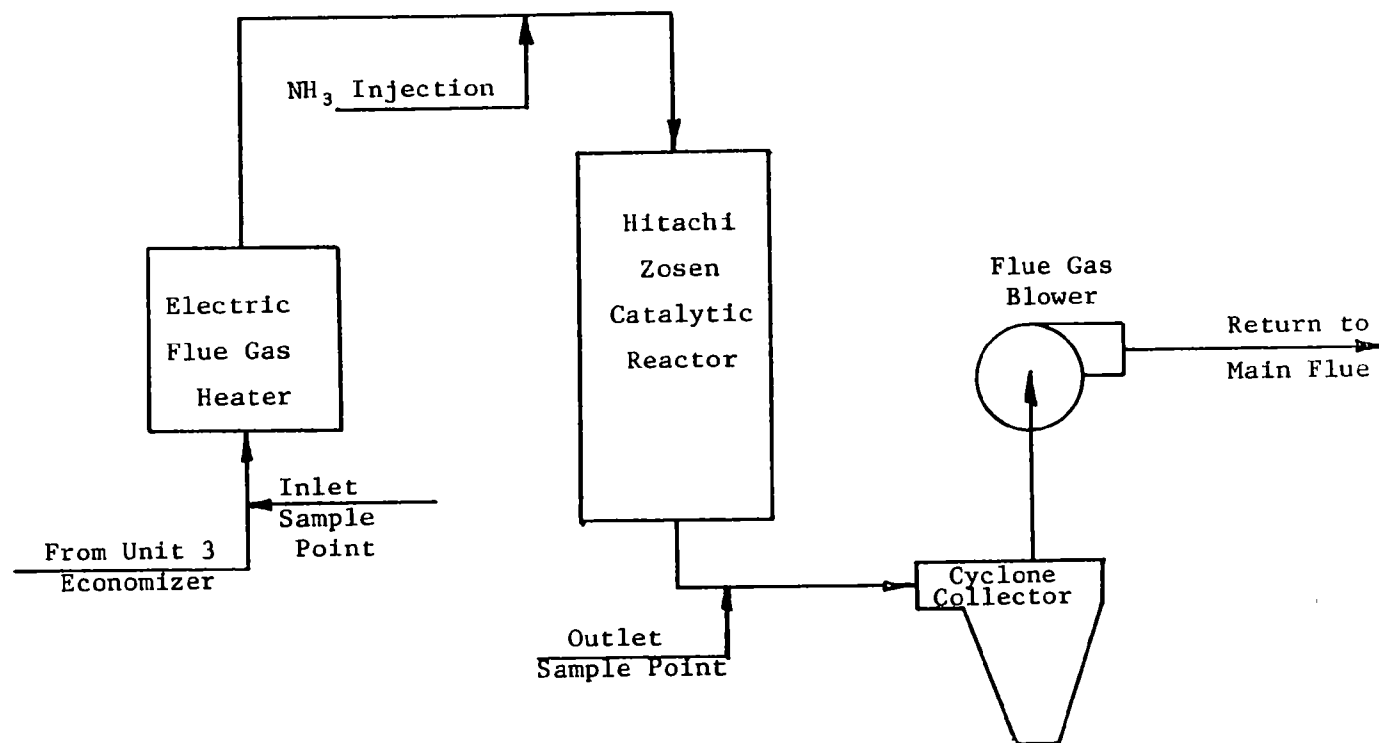
Figure 3-1.  Schematic of the Hitachi Zosen pilot unit.

on the pilot plant, but the parameters measured by these instruments are
sufficient to quantify the plant's performance.

TABLE 3-2.  PRIMARY INSTRUMENTS ON THE HZ PILOT PLANT

| Parameter | Instrument | Location |
|---|---|---|
| Flue Gas Flow Rate | Venturi | Reactor Outlet |
| Flue Gas Temperature | Thermocouple | Reactor Inlet/Outlet |
| $NH_3$ Flow Rate | Rotameter | Reactor Inlet |
| Flue Gas $NO_x$ Concentration | TECO 10 AR Chemilumi-nescent | Reactor Inlet/Outlet |
| Flue Gas $SO_2$ Concentration | TECO 40 Pulsed Fluorescent | Reactor Inlet or Outlet |
| Flue Gas $O_2$ Concentration | Leads and Northrup 7863 Paramagnetic | Reactor Inlet |
| Reactor Pressure Drop | Differential Pressure Flow Transmitter | |

Chemico had originally planned to have a continuous $NH_3$ monitor in the system
to quantify $NH_3$ emissions from the reactor.  However, this monitor never
performed accurately as $NH_3$ reacted with $SO_3$ in the reactor outlet sample
line (see Equations 3-4 and 3-5) thus giving a lower than actual reading.

The controlling consideration of the pilot plant operation was protecting
the catalyst from being damaged or plugged.  The basic precept of start-up
and shutdown procedures was to never expose the catalyst to flue gas or $NH_3$
when the catalyst temperature was less than 230°C.  To initiate a cold start-
up, the electric heater and the induced draft fan were started.  The flue
gas valves on the boiler duct were in the closed position and the air intake
valve was in the open position).  Heated air was drawn through the catalyst
until the catalyst temperature was 230°C.  At this point, the valving was
switched so that the pilot plant was receiving flue gas from the boiler duct.
When the catalyst temperature reached 315°C, then $NH_3$ injection was begun
and testing began.

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During continuous pilot plant operations, a soot blower was used to keep the catalyst surface clean of accumulated fly ash. This was initially performed on an occasional basis using pressurized steam. Later, the frequency was increased to once per shift. By the end of the program, compressed air was being used at least once (often twice) per shift for soot blowing purposes. This is discussed further in Section 4.

To shut down the pilot plant, first the $NH_3$ flow was stopped. Then initial cooling was begun. At approximately 315°C, the pilot plant was switched from flue gas to air and the reactor was purged with hot air before cooling down completely. If the shutdown was due to a temporary outage such as boiler maintenance, hot air ($\sim$200-250°C) would continue to be recirculated through the catalyst via the pilot plant's recycle line.

## 3.3 HITACHI-ZOSEN PILOT PLANT TEST PROGRAM

Testing of the HZ pilot plant was begun in August 1979 and completed in January 1981. The pilot plant was operated for a total of over 10,000 hours using three different catalyst charges (approximately 2500 hours on the first charge, 2300 hours on the second, and 5500 hours on the third). The test program can be divided into two parts, optimization tests and demonstration or long-term tests. The purpose of the optimization tests was to determine the best values of the controlling process parameters (e.g., $NH_3/NO_x$ injection ratio) resulting in the desired $NO_x$ reduction efficiency of 90%. The primary purpose of the demonstration tests was to show the HZ process to be capable of continuously reducing $NO_x$ emissions from a coal-fired boiler for an extended time period. Another important goal of the demonstration tests was to quantify the material and utility demands of the process operating at 90% $NO_x$ reduction efficiency. The following discussion presents a brief operating history of the HZ pilot plant including a discussion of each batch of catalyst tested. Section 4 presents a detailed discussion and interpreation of test results.

## 3.3.1  Optimization Tests - Objectives

The objectives of the optimization tests conducted by Chemico were to quantify the effect of key process operating parameters on the $NO_x$ reduction efficiency of the HZ process and to determine the optimum value of process control parameters required to achieve 90 percent $NO_x$ reduction.

The principal variables examined in the optimization tests were:

- $NH_3/NO_x$ injection ratio,

- Flue gas flowrate,

- Reactor operating temperature, and

- Inlet $NO_x$ concentration.

The effect of each of these variables on the performance of the HZ process can vary in magnitude and direction. The following discussion briefly examines each variable and identifies its directional impact on $NO_x$ reduction efficiency.

### $NH_3/NO_x$ Injection Ratio

The amount of $NH_3$ injected into the flue gas is the primary independent variable which determines the amount of $NO_x$ removed by the SCR system. The $NH_3/NO_x$ mole ratio is the ratio of moles of $NH_3$ injected per mole of $NO_x$ in the flue gas at the reactor inlet. If no $NH_3$ is injected, the mole ratio is obviously zero and no $NO_x$ reduction occurs. As the $NH_3/NO_x$ mole ratio is increased from zero to approximately 0.9 to 1.0 there is a parallel increase in $NO_x$ reduction by the HZ process. At $NH_3/NO_x$ mole ratios of 0.9-1.0, the HZ process achieves approximately 90% $NO_x$ reduction. As the mole ratio is increased beyond this range, the $NO_x$ reduction gradually approaches its theoretically limiting value of 100%. However, for each additional amount of $NH_3$ added beyond the 0.9-1.0 mole ratio range, it is reducing correspondingly less $NO_x$ thus resulting in more unreacted $NH_3$ exiting the reactor as a potential emission.

## Flue Gas Flow Rate

Flue gas flow rate can potentially impact the $NO_x$ reduction efficiency of the HZ process in two ways. An increase in flow rate will reduce the residence time of the flue gas in the reactor. So, if the $NO_x$ reduction efficiency of the system is limited by chemical reaction kinetics, an increase in flow rate will result in a decrease in $NO_x$ reduction. However, if the $NO_x$ reduction efficiency of the system is limited by mass transfer (this refers to the rate of transfer, or diffusion, of the reactants out of the bulk gas to the catalyst surface), then an increase in flow rate may not result in a decrease in $NO_x$ reduction. For the range of flow rates tested at the HZ/Chemico pilot plant, there was little change in the $NO_x$ reduction efficiency of the system for a significant change in flow rate. This suggests that for the design of this pilot plant, the system is not limited by reaction kinetics.

## Reactor Operating Temperature

The reaction temperature can affect the $NO_x$ reduction performance of the HZ process. As the system temperature increases the $NO_x$ reduction efficiency increases due to an increase in the chemical reaction kinetics and the diffusion rate of the reactant species. As the temperature increases beyond the 750-800°F range, the rate of the $NH_3$ oxidation reaction increases thus reducing the overall $NO_x$ reduction. As discussed earlier, at temperatures below about 600°F the rate of the $NO_x$ reduction reactions decrease and the formation of ammonium sulfates becomes a potential problem.

## Inlet $NO_x$ Concentration

Another process parameter that was investigated to determine its impact on the system $NO_x$ reduction performance was inlet $NO_x$ concentration. While this parameter is not directly controllable in a commercial situation, provisions were made as part of this pilot program to "spike" the flue gas with $NO_x$ to determine the effect of high $NO_x$ concentrations. While there was a

slight increase in $NO_x$ reduction, it was concluded that high inlet $NO_x$ concentrations will not adversely affect the processes removal efficiency.

### 3.3.2 Optimization Tests - History

Optimization tests were conducted for each of the three charges of catalyst installed in the HZ pilot plant, while the 90 day demonstration test was conducted with the third catalyst. The following discussion summarizes the optimization tests conducted on each charge of catalyst. This includes a summary of the total time flue gas was processed by each catalyst.

### Catalyst Charge 1

The first catalyst charge was installed in the reactor in August 1979. Shortly after catalyst installation the pilot plant was started up and then exposed to flue gas. The optimization tests on this catalyst charge were plagued by a series of minor problems, the type of which often occur during the initial phases of pilot plant operation. In August, there were several shutdowns due to leaks in the inlet sample line and leaks in the flanges around the reactor. Very little testing was performed in September due to analyzer problems and a two week boiler outage. Testing was delayed in October due to malfunctions in the flowmeter (and its spare) that was used to control the $NH_3$ injection rate. Also, the continuous analyzer for $NH_3$ emissions from the reactor outlet did not work properly. It was then decided to use a grab sampling/wet chemical analysis method for $NH_3$ emission monitoring instead of the continuous analyzer. In November the plant was shut down to revise the ductwork around the reactor to prevent fly ash buildup, install an $NH_3$ distributor (two crossed pipes with orifices in them), and clean the catalyst.

After the initial system debugging work, the optimization test for the effect of $NO_x$ concentration showed that the inlet $NO_x$ concentration had little or no effect on $NO_x$ reduction efficiency. During the $NH_3/NO_x$ mole ratio and the flue gas flow rate tests it became apparent that the catalyst performance

was decreasing since the percentage $NO_x$ reduction decreased and the reactor pressure drop increased. Because of this, the pilot plant was shut down again and the reactor was opened. The catalyst was taken out and cleaned. When the catalyst was replaced the pressure drop returned to normal but the $NO_x$ reduction was still lower. It became apparent that the activity of the catalyst had decreased enough so that 90 percent $NO_x$ reduction could not be maintained; therefore, HZ decided to replace the catalyst. At this point the reactor had processed flue gas for approximately 2500 hours.

## Catalyst Charge 2

The second charge of catalyst was installed in the reactor in December 1979. It had the same composition, volume, and pitch (size of the gas passages) as the first catalyst, but because of the plugging problems experienced with the first catalyst, HZ modified pilot plant operation to include steam soot blowing once per shift.

Optimization tests with the new catalyst charge were begun after installation in December 1979. These tests were intended to determine the effects of $NH_3/NO_x$ mole ratio, flue gas flow rate, and reaction temperature on $NO_x$ reduction efficiency and the amount of $NH_3$ exiting the reactor.

The optimization tests on catalyst charge #2 were characterized by unexpectedly high $NO_x$ reduction efficiencies. It was determined later that particles of catalyst had become imbedded in the outlet analyzer probe. As a result, the probe was functioning as a catalytic reactor reducing $NO_x$ and then giving artifically low outlet $NO_x$ concentrations resulting in high calculated $NO_x$ reduction efficiencies. The problem was corrected by replacing the probe and periodically checking it for catalytic activity. The results of the optimization tests identified the conditions at which the pilot plant would operate during the demonstration test. These conditions are summarized in Table 3-3.

TABLE 3-3.  RESULTS OF OPTIMIZATION TESTS ON CATALYST CHARGE #2

| Parameter | Value |
|---|---|
| $NH_3/NO_x$ Mole Ratio | 1.0 |
| Flue Gas Flow Rate | 1050 scfm |
| Flue Gas Temperature | 700°F |
| $NO_x$ Reduction Efficiency | 92% |

As efforts were made to begin the final phase of the project, a continuous long-term run under optimum conditions, the $NO_x$ reduction efficiency dropped unexpectedly.  This phenomenon was similar to the experience with the first catalyst charge as the decrease in efficiency occurred after a plant shut down and was accompanied by a large increase in reactor pressure drop. The shutdown (to replace flue gas heater elements) and start-up had followed the prescribed procedures:  the catalyst was never in contact with flue gas or $NH_3$ at temperatures less than 230°C.  The reactor was completely purged with hot air before cooling.  On start-up, hot air was used to heat the catalyst to 230°C.  Flue gas was then introduced and the temperature raised to 315°C at which point $NH_3$ was introduced.  Numerous attempts were made to clean the catalyst:  increasing soot blowing pressure and frequency, passing hot air through the catalyst, and removing the catalyst to clean it physically and with compressed air.  None of these efforts were successful.  HZ then decided to replace the catalyst with a new charge.  At this point the second catalyst had processed flue gas for approximately 2300 hours.

When the second catalyst was removed from the reactor, physical examination revealed that many of the gas passages had become obstructed by agglomerated deposits of fly ash.  Initially, it was suspected that the steam used for soot blowing was adding moisture to the reactor and resulted in fly ash agglomeration.  For this reason, HZ decided to use compressed air for soot blowing in future tests.  Subsequent examination of the fly ash, however, indicated that the ash had a tendency to agglomerate without any additional moisture being present.

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## Catalyst Charge 3

The third catalyst charge was of a different type than the first two charges. This catalyst had somewhat different characteristics, primarily a wider pitch (spacing between plates) to help prevent plugging by fly ash. The wider pitch of this catalyst necessitated a longer catalyst bed to provide the same amount of surface area, so the reactor had to be lengthened. After this work had been completed, the pilot plant was started up with the third catalyst charge in May 1980.

The results of the optimization tests on the third catalyst charge are summarized in Table 3-4.

TABLE 3-4. RESULTS OF OPTIMIZATION TESTS ON CATALYST CHARGE #3

| Parameter | Value |
|---|---|
| $NH_3/NO_x$ Mole Ratio | 1.0 |
| Flue Gas Flow Rate | 1500 scfm |
| Flue Gas Temperature | 700°F |
| $NO_x$ Reduction Efficiency | 93% |

Low flue gas flow rate tests were postponed because of a slight increase in reactor pressure drop during the first test. Because of the plugging problems experienced with the first two catalyst charges, it was decided to run the long-term demonstration test at a higher flow rate to attempt to keep the catalyst surface cleaner via the increased gas turbulence. $NO_x$ removals at the higher flow rates were above 90 percent so the demonstration test was initiated in June 1980.

### 3.3.3 Demonstration Test

One of the main purposes of this pilot plant program was to operate the HZ process continuously for a period of 90 days. The primary objective of this demonstration test was to achieve a daily average $NO_x$ reduction of

90 percent for at least 75 out of 90 days. The initial 90-day demonstration test at the HZ pilot plant began in May 1980 and continued through August 1980. During this 90-day period, only 75 days of data were obtained due to malfunctions of the outlet $NO_x$ analyzer which required repairs. Out of these 75 reporting days there were 57 daily average $NO_x$ reduction efficiencies of 90 percent or greater. Average values of the descriptive process parameters for the 90-day demonstration test are listed in Table 3-5.

TABLE 3-5. RESULTS OF 90-DAY DEMONSTRATION TEST: MAY-AUGUST 1980

| Parameter | Average Value |
|---|---|
| $NH_3/NO_x$ Mole Ratio | 0.98 |
| Flue Gas Flow Rate | 1410 scfm |
| Flue Gas Temperature | 713°F |
| $NO_x$ Reduction Efficiency | 90.7% |
| Inlet $NO_x$ Concentration | 452 ppm |
| $NH_3$ Emissions | 53 ppm |

Because of the success of the initial 90-day test period, the demonstration test was extended. A major objective during the extended test period was to determine the long-term effects of exposure to coal-fired flue gas on catalyst activity. The $NO_x$ reduction performance of the system decreased slightly, by about 2.5%, during the period from August to October 1980. At approximately the same inlet conditions, the average $NO_x$ removal for this period was 88.3%. The results of the long-term demonstration test through October are listed in Table 3-6.

TABLE 3-6.  RESULTS OF LONG-TERM DEMONSTRATION TEST:  MAY-OCTOBER 1980

| Parameter | Average Value |
|---|---|
| $NH_3/NO_x$ Mole Ratio | 0.98 |
| Flue Gas Flow Rate | 1370 scfm |
| Flue Gas Temperature | 701°F |
| $NO_x$ Reduction Efficiency | 89.8% |
| Inlet $NO_x$ Concentration | 451 ppm |
| $NH_3$ Emissions | 57 ppm |

For this approximately 5 month period, out of 144 calendar days there were 118 days of reported data.  Again, the 26 days where no data were reported were characterized by boiler outages and analyzer breakdowns. Of these 118 reporting days, 63 days (over 50%) had average $NO_x$ reductions of 90 percent or greater.

## 3.4  INDEPENDENT EVALUATION OF THE HZ PROCESS

Radian Corporation conducted a sampling test program at the HZ pilot plant to enable an independent evaluation of the HZ process.  This program featured the three following areas of testing:

- Quality Assurance
- Continuous $NO_x$ Monitor Certification
- Stack Sampling (secondary emissions)

This independent evaluation test program was performed during July and August 1980, the later stages of the initial 90-day demonstration test on the third catalyst charge.

The following discussion presents the test plans for each area of the independent evaluation.  The results of this evaluation are presented in Section 4.

## 3.4.1 Quality Assurance

An independent quality assurance program was conducted by Radian at the HZ pilot plant to ensure the accuracy of the process measurements made by Chemico. The measurements audited were those that are necessary to characterize the performance of the HZ process, quantify raw material and utility demands, and permit a technical evaluation of the HZ process for a commercial installation. Those process measurements audited by Radian and their frequencies are listed in Table 3-7.

TABLE 3-7. AUDITS OF THE PROCESS MEASUREMENTS AT
THE HITACHI-ZOSEN PILOT PLANT

| Process Measurement | Audits/Week |
|---|---|
| $NH_3$ Injection Rate | 1 |
| Reactor Pressure Drop | 2 |
| Flue Gas Flow Rate | 2.5 |
| $NH_3$ Emissions | 3 |
| Reactor Inlet Temperature | 1 |

The results of the quality assurance audits and the procedures used are presented in Appendix A. A summary and discussion of these results appears in Section 4.

## 3.4.2 Continuous $NO_x$ Monitor Certification

One of the most critical aspects of the independent evaluation test program was to certify the continuous monitors that measured the reactor inlet and outlet $NO_x$ concentrations. The procedures used have been developed by EPA to ensure the accuracy of continuous monitors at facilities which must meet new source performance standards. A continuous monitor must pass a number of tests which include:

- relative accuracy,
- calibration error,
- response time,
- 2- and 24-hour calibration drift, and
- 2- and 24-hour zero drift.

The specifications for these tests are in the Federal Register, Vol. 44, No. 197, October 10, 1979 - "Proposed Rules: Standards of Performance for New Stationary Sources; Continuous Monitoring Performance Specifications." These specifications are listed in Table 3-8.

These certification tests are discussed here and results are summarized in Section 4.

TABLE 3-8.  CONTINUOUS MONITOR CERTIFICATION TESTS

| Certification Test | Performance Specifications |
| --- | --- |
| Relative Accuracy | $\leq 20$ percent of reference methods test data in terms of emission standard expressed in mass per unit heat input |
| Calibration Error | $\leq 5$ percent for mid-range and high level calibration values |
| Response Time | $\leq 15$ minutes |
| Calibration Drift (2-hour) | $\leq 2$ percent of span value |
| Calibration Drift (24-hour) | $\leq 2.5$ percent of span value |
| Zero Drift (2-hour) | $\leq 2$ percent of span value |
| Zero Drift (24-hour) | $\leq 2.5$ percent of span value |

Relative Accuracy

Relative accuracy is the most important test of the continuous $NO_x$ monitors performance. This test is a comparison of the continuous monitors readings with a stack gas analysis as determined by EPA reference methods: Method 7 for $NO_x$ and Method 3 for $O_2$ and $CO_2$. Nine Method 7 tests are made,

requiring three samples per test and the results are compared to the readings of the continuous $NO_x$ monitor during the time the stack gas samples were collected. Simultaneous Method 3 tests are performed so the $NO_x$ concentrations can be converted to a mass emissions per unit heat input basis. Then, the relative accuracy is calculated by using the following equations.

$$\text{Relative Accuracy} = \frac{|\bar{X}| + |C.I._{.95}|}{R.V.} \tag{3-7}$$

where $|\bar{X}|$ = absolute value of the mean difference between the monitor reading and the average value of the Method 7 tests,

$R.V.$ = average $NO_x$ concentration of the Method 7 tests,

$|C.I._{.95}|$ = absolute value of the 95 percent confidence interval which is defined by Equation 3-8.

$$C.I._{.95} = \frac{t_{.975}}{n(n-1)^{\frac{1}{2}}} (n \Sigma X_i^2 - (\Sigma X_i)^2)^{\frac{1}{2}} \tag{3-8}$$

where n = number of measurements (9),

$t_{.975}$ = 2.306 for 9 tests,

$X_i$ = difference between the continuous monitor reading and the Method 7 test result.

This procedure was followed exactly at the HZ pilot plant.

Calibration Error

Calibration error is a measure of the continuous monitor's ability to accurately measure the concentration of a calibration gas. A series of 15 measurements are made, 5 each of high- and mid-level calibration gases and 5 of zero gas (air). The measurements are made such that no gas is measured two or more times in a row. The calibration error is determined using Equations 3-7 and 3-8 where the R.V., the reference value, is equal to the calibration gas concentration and $t_{.975}$ = 2.776 (for 5 measurements). This procedure was followed exactly at the HZ pilot plant.

## Response Time

Response time measures the amount of time before a continuous monitor responds to a change in the $NO_x$ concentration in the duct. Zero gas (air) is introduced into the continuous $NO_x$ monitor's sample line at the duct. When the reading stabilizes at zero, the system is switched to monitor the flue gas and the time required to reach a stable value is the upscale response time. Downscale response time begins with high-level calibration gas and the procedure is repeated.

## Zero and Calibration Drift

Zero and calibration drift are measures of the change of the continuous $NO_x$ monitor's response to zero and calibration gases with time. For the two-hour drift test, zero and high level span gases are passed into the monitor every two hours. The difference between the reading and the zero or calibration gas concentrations is recorded. Fifteen sets of data are taken. Drift is calculated using Equations 3-7 and 3-8 where the reference value (R.V.) is equal to the monitor range and $t_{.975} = 2.145$ for 15 tests. 24-drift is measured similarly in 7 tests where $t_{.975} = 2.447$.

Since this pilot plant was an experimental unit, it was crucial for the monitors to be accurate; therefore, they were calibrated every two hours, sometimes even more frequently. The 24-hour drift test was irrelevant to the operation of this pilot plant. Zero and calibration drift readings were measured prior to Chemico's routine calibration.

Detailed results of the continuous monitor certification tests are presented in Appendix B while a summary of the results is presented in Section 4.

## 3.4.3 Stack Sampling for Secondary Emissions

In this study, $NO_x$ emissions are of primary interest; however, emissions of other compounds are also important. These were termed secondary emissions and the sampling for these compounds was a part of the independent evaluation test program. The objective was to quantify any change in concentration due to passing across the HZ catalyst. Table 3-9 lists the pollutants and the sampling plan of the secondary emission testing.

TABLE 3-9. SECONDARY EMISSIONS TESTING

| Pollutant | Sampling Location | Number of samples at each location |
|-----------|-------------------|------------------------------------|
| Particulate Matter Loading | Reactor Inlet/Outlet | 3 |
| Particulate Matter Composition | " | 3 |
| Sulfur Trioxide ($SO_3$) | " | 6 |
| Carbon Monoxide (CO) | " | 3 |
| Hydrocarbons ($C_1-C_6$) | " | 3 |
| Hydrogen Cyanide (HCN) | " | 3 |
| Nitrosoamines | " | 3 |
| Nitrous Oxide ($N_2O$) | " | 3 |

Particulate matter loading was measured to quantify the loading of fly ash to which the catalyst was exposed. This would demonstrate the catalyst's capability to operate under high fly ash loading conditions. Particulate matter composition was analyzed to determine if catalyst erosion caused a measurable change in particulate composition. The composition was analyzed for any increase in titanium or vanadium (primary components of the HZ catalyst) concentration at the reactor outlet.

SO$_3$ concentration in the flue gas was measured to quantify any production of SO$_3$ due to SO$_2$ oxidation by the catalyst. Some degree of SO$_2$ oxidation was expected as vanadium pentoxide is the catalyst used commercially to oxidize SO$_2$ to SO$_3$ in sulfuric acid plants.

Carbon monoxide and hydrocarbons were measured to determine any change in concentration across the reactor. Since they both can be oxidized by oxygen or NO$_x$, it is possible that their concentrations might be reduced.

Hydrogen cyanide, nitrosoamines, and nitrous oxide were measured to determine any change in concentration across the reactor. While no test results indicate that these compounds are produced by SCR processes, there are concerns that NH$_3$ in the presence of the catalyst might result in the production of one or more of the compounds.

The analyses of samples (except for nitrosoamines) was conducted onsite to give quick feedback in case of unusual results. The sampling and analysis procedures and their results are given in Appendix C. A summary of the results appears in Section 4.

# SECTION 4

## HITACHI ZOSEN PILOT PLANT TEST RESULTS

The HZ pilot plant tests conducted by Chemico and the independent process evaluation test program performed by Radian were designed to assess the technical feasibility of the HZ process and allow more accurate cost estimates to be made. The results of these test programs were utilized to produce a conceptual design for a commercial application of the HZ process. This section summarizes and discusses the most significant results of the test program.

Test data are presented in this section as singular data points; however, they do not represent a single test. Instead, they represent the average of data collected at specific performance levels. For example, where $NO_x$ removal is presented for a particular temperature, mole ratio and flow rate, the $NO_x$ removal number represents the average of all appropriate tests at these conditions. Likewise, the temperature, mole ratio and flow rate represent averages of data lying within a specified range.

More detailed results of Radian's test program are contained in the Appendices. Detailed results from the Chemico test program are contained in the final report prepared by Chemico and Hitachi Zosen.

In the sections which follow, the test results of each phase of testing are discussed separately. The sections are organized in the following order:

- Optimization Tests,

- Demonstration Tests,

- Quality Assurance Audits,

- Continuous $NO_x$ Monitor Certification Tests, and

- Stack Sampling for Secondary Emissions.


## 4.1 OPTIMIZATION TESTS

Optimization tests conducted by Chemico were intended to determine the optimum values of the controlling process parameters to obtain 90% $NO_x$ reduction. The parameters of interest were as follows:

- Flue Gas Temperature,

- Flue Gas Flow Rate, and

- $NH_3/NO_x$ Mole Ratio.

Optimization tests had been initiated on the first catalyst charge and completed on the second catalyst charge, both of which were the NOXNON 500 series. It was determined from these tests that the flue gas temperature did not have a strong effect on $NO_x$ reduction, within the normal operating temperature range of the catalyst (300 to 400°C). As the flue gas temperature approached 430°C, there was a slight decrease in $NO_x$ reduction probably due to increased $NH_3$ oxidation. As the flue gas temperature drops below 340°C, the $NO_x$ reduction decreases due to slower reaction rates.

Some of the temperature optimization test results are presented in Table 4-1.

TABLE 4-1. SUMMARY OF TEMPERATURE OPTIMIZATION TEST RESULTS

| Flue Gas Flow Rate (scfm) | $NH_3/NO_x$ Mole Ratio | Flue Gas Temperature (°C) | $NO_x$ Reduction (%) |
|---|---|---|---|
| 1050 | .91 | 410 | 92 |
| 1050 | .89 | 378 | 94 |
| 1050 | .92 | 339 | 91 |

These results indicate that $NO_x$ reduction is not a strong function of temperature. Therefore, for commercial operations temperature need not be controlled as long as it remains in the 340 to 410°C temperature range.

The flue gas flow rate optimization tests showed that an increase in flow rate results in a slight decrease in $NO_x$ reduction efficiency. These results are shown in Figure 4-1. While there is a slight decrease in percent $NO_x$ reduction with increased flow rate, the rate of the $NO_x$ reduction reactions increases significantly. This is probably due to enhanced mass transfer which can occur as a result of increased gas turbulence in the reactor. There is an economic tradeoff between increased flue gas flow rate (effectively reducing the amount of catalyst required per unit mass of $NO_x$ removed) and increased reactor pressure drop. A good commercial design should provide the reactor with the capability of handling the maximum anticipated flow rate. Then, at lower flow rates, as could occur during low load operation, the percent $NO_x$ reduction would not decrease.

The $NH_3/NO_x$ mole ratio optimization tests were designed to quantify the effect of $NH_3/NO_x$ injection ratio on $NO_x$ reduction. With the flue gas temperature and flue gas flow rate held constant, the $NH_3/NO_x$ injection ratio was varied and the resulting $NO_x$ reduction was measured. Results of these $NH_3/NO_x$ mole ratio tests are shown in Figure 4-2. Also, Figure 4-2 shows the magnitude of $NH_3$ emissions exiting the HZ reactor. These results were determined by stack sampling tests conducted individually by both Chemico and Radian. At lower $NH_3/NO_x$ mole ratios, an increase in the mole ratio results in significant increase in $NO_x$ reduction with only a moderate increase in $NH_3$ emissions. However, at higher mole ratios less additional $NO_x$ reduction is achieved and $NH_3$ emissions significantly increase when the mole ratio is increased.

## 4.2 DEMONSTRATION TEST RESULTS

The primary objective of the demonstration test at the HZ pilot plant was to reduce $NO_x$ emissions by 90% continuously for 90 days. This demonstration test began in May 1980 and since it was successful, was extended 5 months beyond the initial 90-day period.
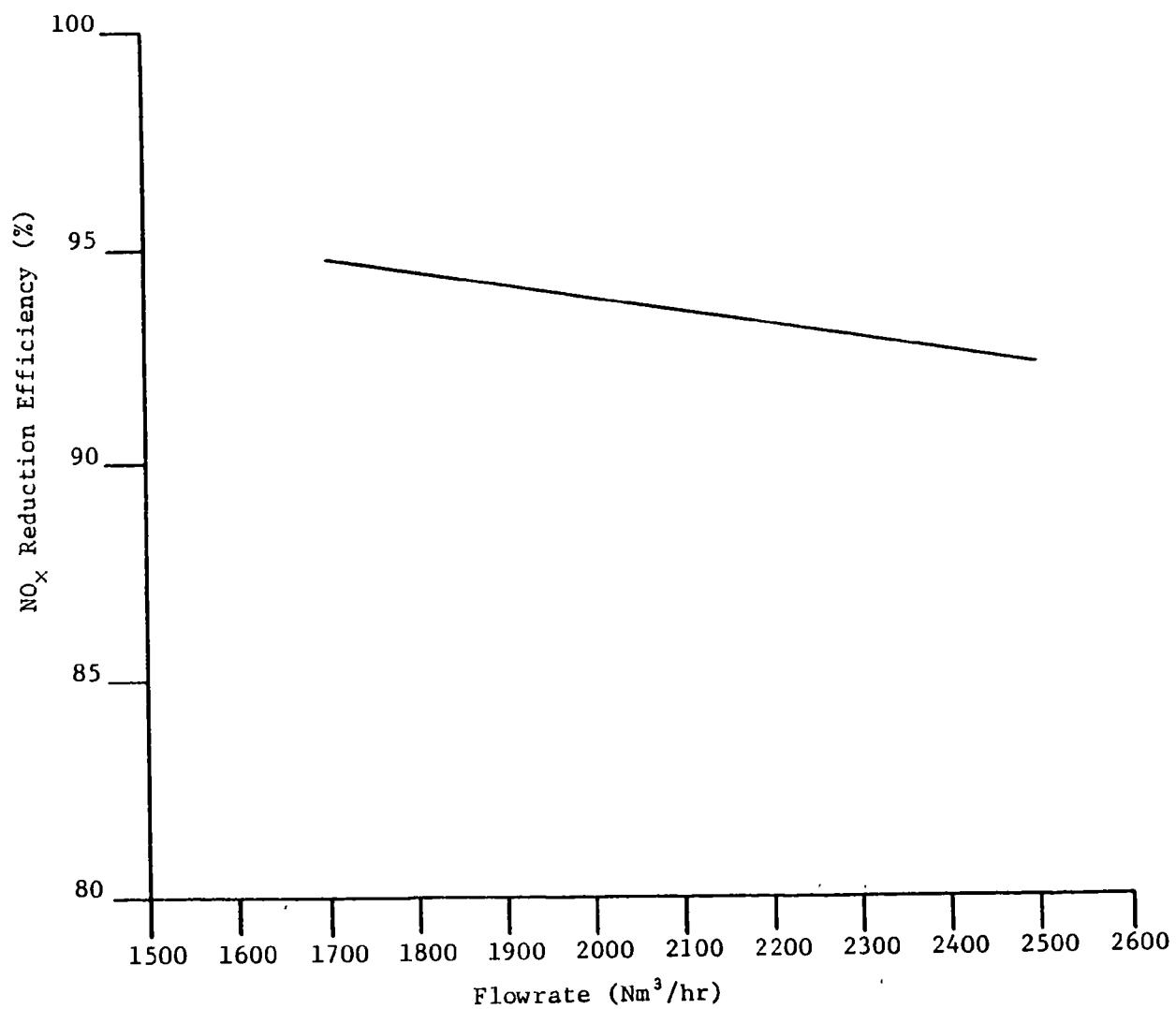
Figure 4-1. NO$_x$ reduction as a function of flue gas flowrate.
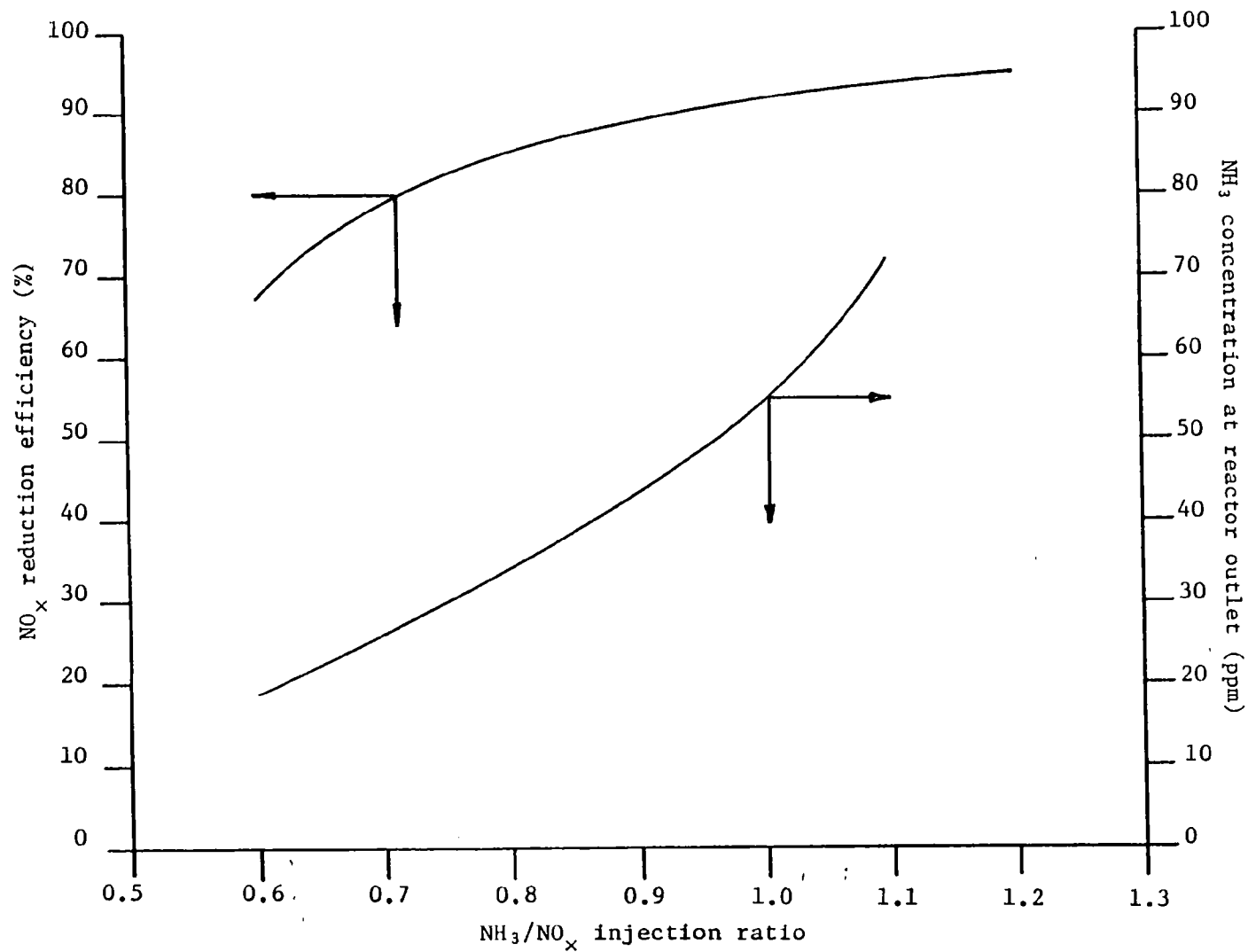
Figure 4-2. $NO_x$ reduction efficiency and $NH_3$ emissions as a function of $NH_3/NO_x$ injection ratio.

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Table 4-2 lists the average values of the key process variables during
the demonstration test.

TABLE 4-2. KEY PROCESS VARIABLE VALUES DURING THE $NO_x$ DEMONSTRATION TEST,
MAY-OCTOBER 1980

| Operating Variable | Average Value | Standard Deviation |
|---|---|---|
| Flue Gas Flow Rate (scfm) | 1370 | 97 |
| Reactor Pressure Drop (in. $H_2O$) | 1.12 | 0.10 |
| Inlet $NO_x$ Concentration (ppm) | 451 | 54 |
| Flue Gas Temperature (°F) | 701 | 24 |
| $NH_3/NO_x$ Mole Ratio | 0.98 | 0.07 |
| $NO_x$ Reduction (%) | 89.8 | 3.8 |
| $NH_3$ Emissions (ppm) | 54 | 15 |

Figures 4-3 and 4-4 graphically show the daily average performance of the
HZ pilot plant. The system successfully met the objective of continuous 90%
$NO_x$ removal of the 90-day demonstration test. However, Figure 4-3 shows that
the $NO_x$ reduction efficiency was slightly decreasing over the 5-month period.
This decrease in $NO_x$ reduction indicates a slight loss of catalyst activity
due to exposure to coal-fired flue gas.

Figure 4-5 shows the estimated relative reactivity of the catalyst as a
function of time. These curves were determined by calculating the $NO_x$
reduction reaction rate at an $NH_3/NO_x$ mole ratio of 1.0 at various times
during the pilot plant's operation. Figure 4-5 shows that after three months
of exposure to coal-fired flue gas, the catalyst reactivity had decreased
by a few percent. Six months of exposure saw yet another decrease in reactivity.
Finally, after nine months of operation, just prior to the final shutdown and
disassembly of the pilot plant, the catalyst reactivity had decreased approxi-
mately 20% relative to its initial performance. At this point an experimental
regeneration technique was implemented in which the catalyst was water-washed
with warm water. This technique returned the catalyst from 77% of its initial

% REMOVAL

100

90

80

70

N H 3 N O X

1.2

1.0

0.8

0.6

*Note: Additional low mole ratio tests were run on these two days.

F L O W scfm

1600

1500

1400

1300

1200

1100

MAY | JUNE | JULY | AUGUST | SEPTEMBER | OCTOBER
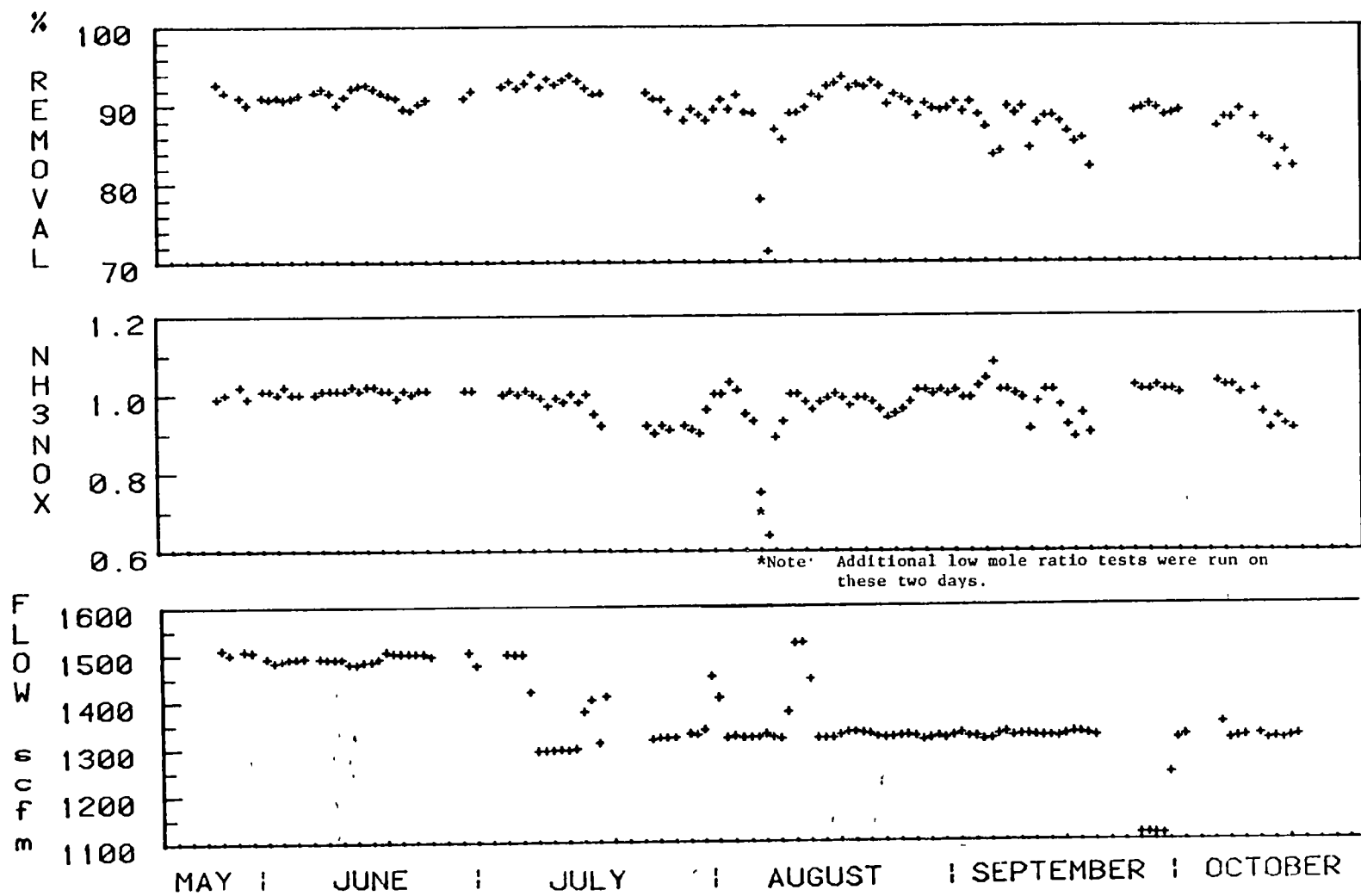
Figure 4-3. Results of $NO_x$ demonstration test of HZ pilot plant.
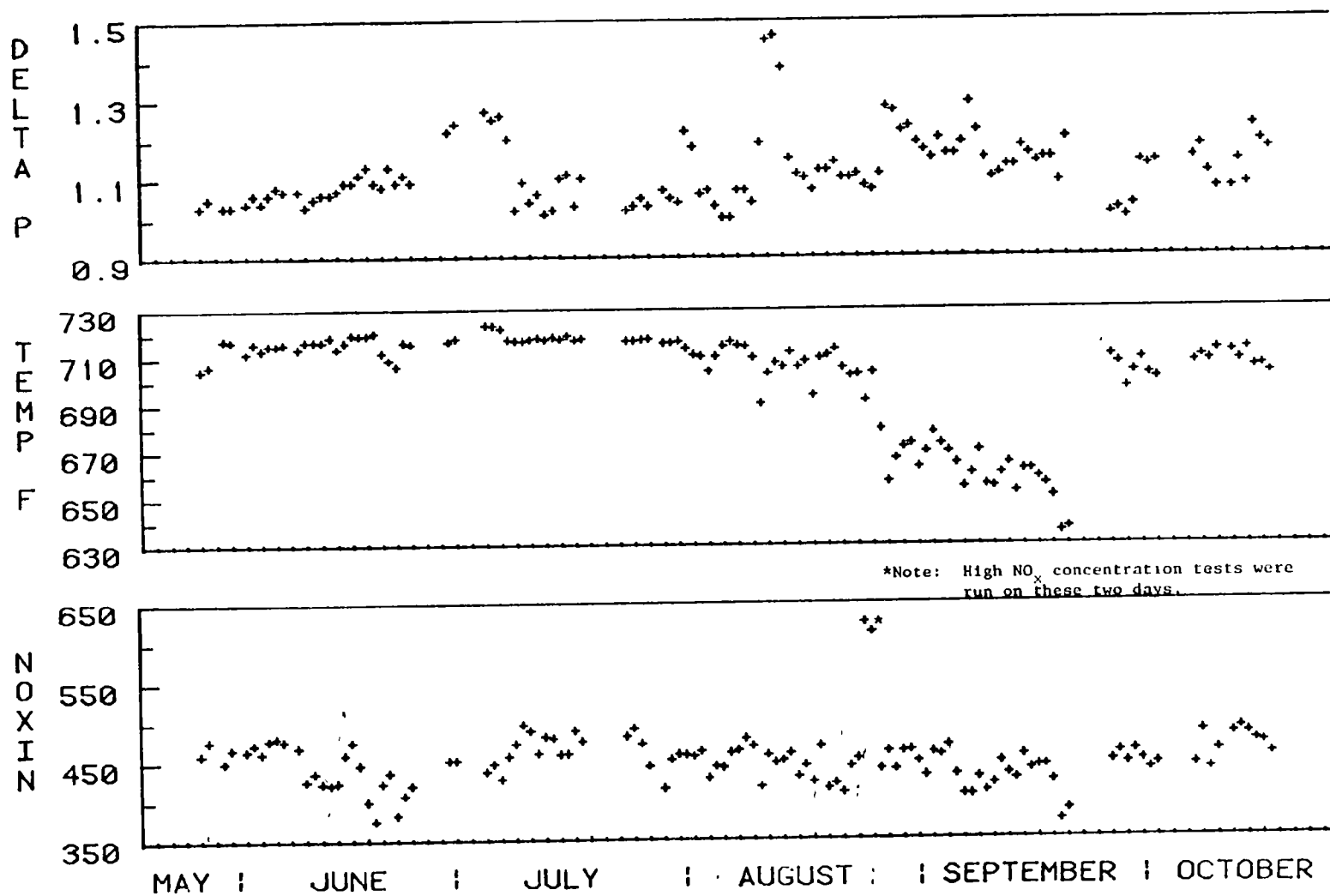
Figure 4-4. Results of demonstration test of HZ pilot plant.
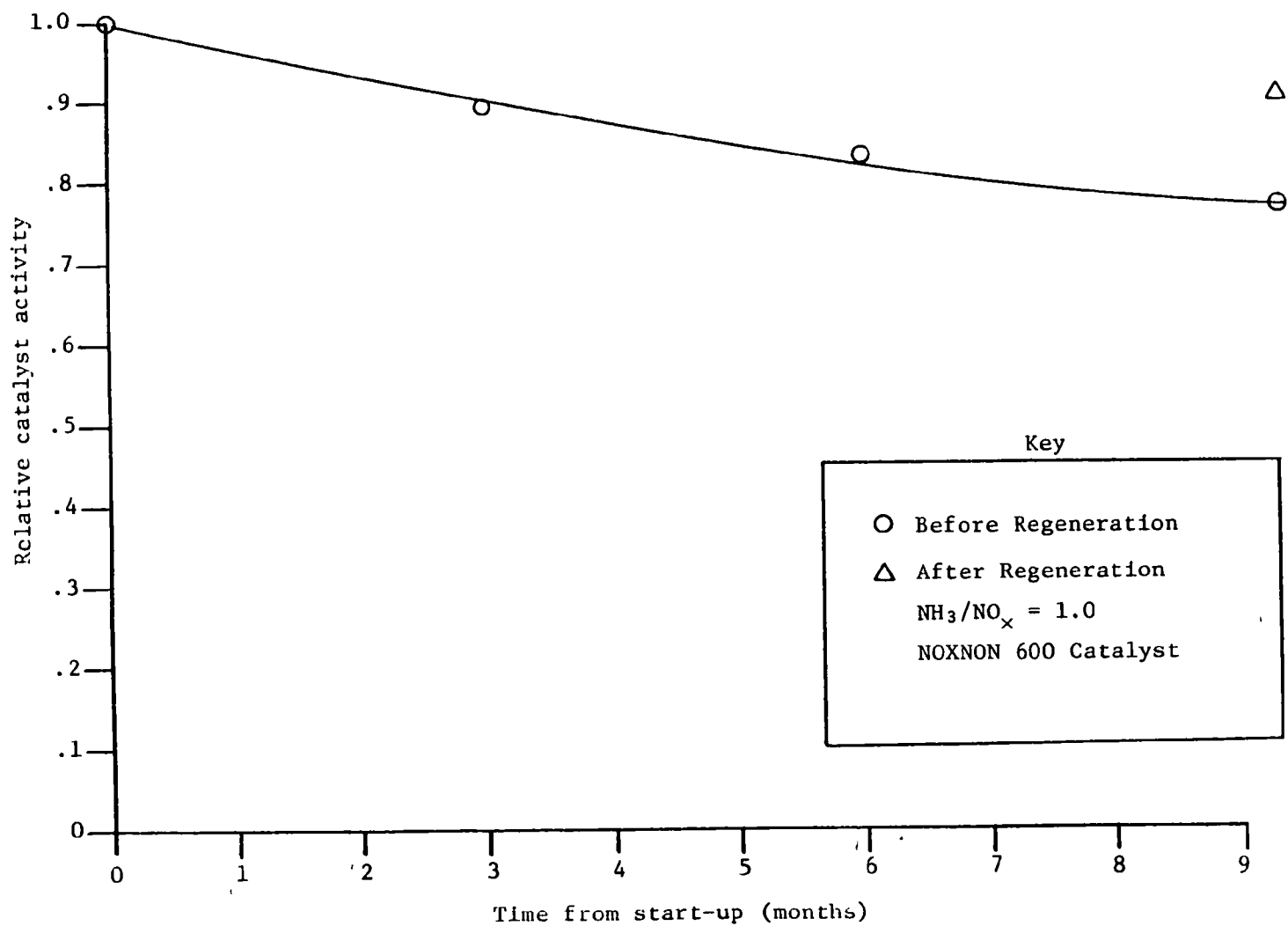
Figure 4-5. Relative catalyst activity vs. time.

activity to 85% of the initial activity.  Although the demonstration test of the HZ pilot plant did not show the process capable of maintaining 90% $NO_x$ reduction for a complete year, the success of the 90-day run and the potential catalyst regeneration technique indicate the process is suited for application to a coal-fired source.

## 4.3 QUALITY ASSURANCE AUDIT TEST RESULTS

The quality assurance audit tests were performed by Radian to ensure that the data collected by Chemico from the pilot demonstration of the HZ process were accurate.  To accomplish this evaluation, Radian used standard reference methods to audit the process variables that characterize the performance of the HZ process and that were monitored continuously by Chemico.  The one variable audited that was not monitored continuously by Chemico was the reactor outlet $NH_3$ concentration.  The pilot plant was originally designed to monitor the $NH_3$ emission rate continuously by using a total nitrogen analyzer. However, the sample gas conditioning system to prevent ammonium sulfate/bisulfate formation (by removing the $SO_3$) never functioned properly.  As a result, Chemico took batch $NH_3$ samples for spectrophotomic analysis on a regular basis.

The results of Radian's $NH_3$ emission tests are listed in Table 4-3.  These tests show an average $NH_3$ emission rate of 55 ppm for an $NH_3/NO_x$ mole ratio of 0.96 with 464 ppm $NO_x$ at the reactor inlet.  This emission rate is significantly higher than the 10-20 ppm expected by Chemico.  This may have been due to an insufficient amount of catalyst or, conversely, an excessive flue gas flow rate, either of which affect the space velocity and hence residence time. Lower ammonia emissions would be anticipated if a lower space velocity was implemented.

TABLE 4-3. HITACHI ZOSEN PILOT PLANT $NH_3$ EMISSIONS

| Test | $NO_x$ In (ppm wet) | $NH_3:NO_x$ | $NH_3$ Emission (ppm dry) |
|------|------|------|------|
| 1 | 459 | 0.91 | 45 |
| 2 | 451 | 0.97 | 46 |
| 3 | 466 | 0.92 | 49 |
| 4 | 453 | 0.92 | 60 |
| 5 | 469 | 0.99 | 44 |
| 6 | 479 | 0.99 | 63 |
| 7 | 440 | 1.05 | 54 |
| 8 | 450 | 0.89 | 58 |
| 9 | 460 | 1.01 | 74* |
| 10 | 493 | 0.89 | 41* |
| 11 | 482 | 0.98 | 68* |
| Average = | 464 | 0.96 | 55 |

*Note: Sample analyzed by pH adjustment, direct nesslerization/spectrophotometry instead of pH adjustment, distillation/titration as for other samples. Tests 4 and 5 were run with both methods with good agreement.

Normalized ammonia emission results from both Radian and Chemico test data are shown in Figure 4-6. $NH_3$ emissions are normalized by dividing by the inlet $NO_x$ concentration. This method of presentation is more useful han the standard $NH_3$ emissions vs. $NH_3/NO_x$ mole ratio plot since it includes the effects of $NO_x$ concentration. $NO_x$ concentration will affect the concentration of ammonia at the reactor outlet (at a constant $NH_3/NO_x$ mole ratio) since an increase of the inlet $NO_x$ concentration produces a corresponding increase in the quantity of $NH_3$ injected and a consequent increase in the quantity of $NH_3$ emitted.

The results of the other QA audits performed by Radian are summarized in Table 4-4. (More detailed results, including the individual audit results, are included in Appendix A). All the QA measurements except the reactor inlet $SO_2$ concentrations were within 10 percent of the measurements made by Chemico.
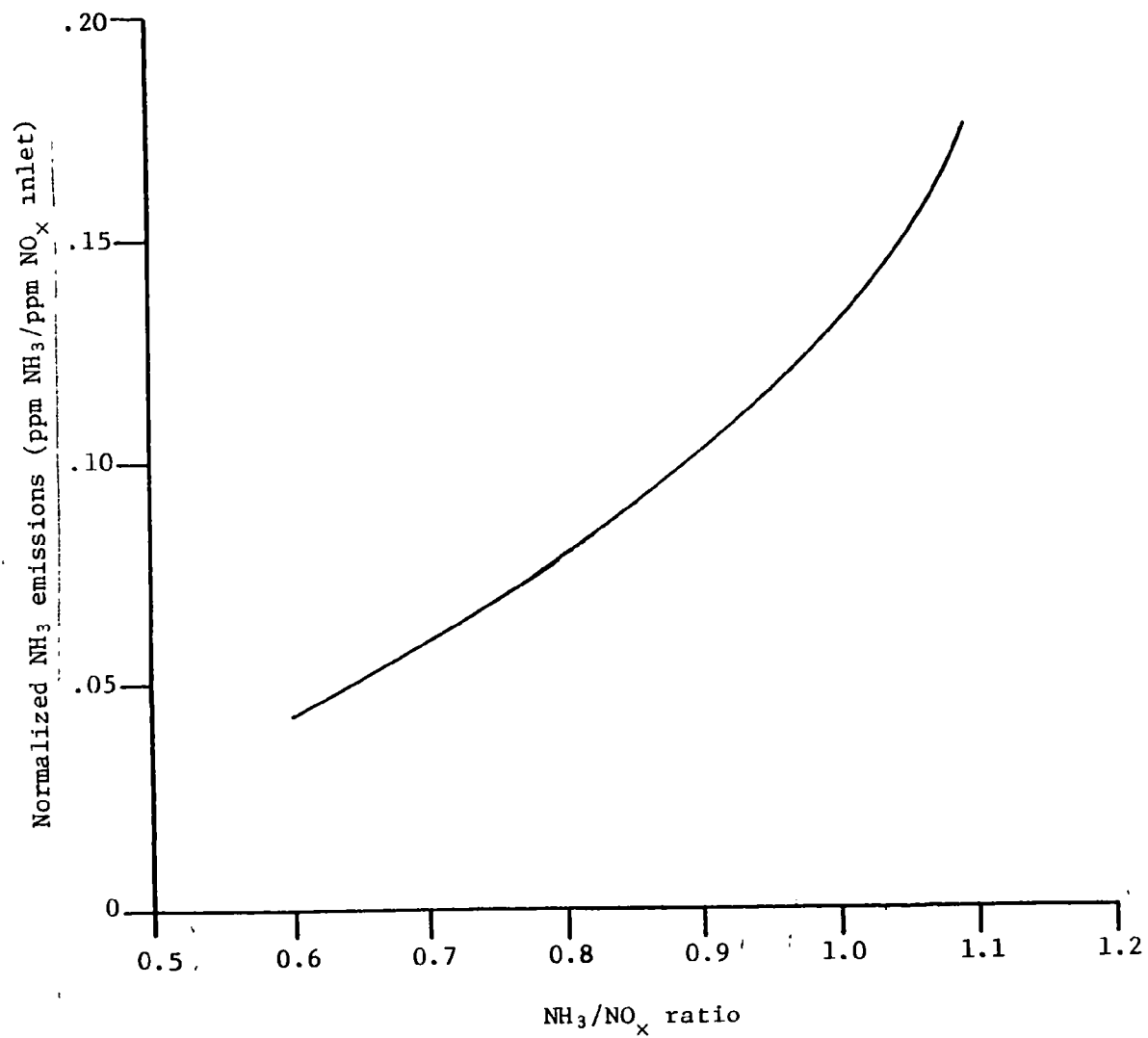
Figure 4-6.  Normalized $NH_3$ emissions as a function of $NH_3/NO_x$ injection ratio.

TABLE 4-4. OTHER QA AUDIT TEST RESULTS

| Process Variable | Audit Method | Relative Error (%)[1] |
|---|---|---|
| Flue Gas Flow Rate | EPA Reference Method 2 | -0.3 |
| $NH_3$ Injection Rate | Absorption in 50% $H_2SO_4$ followed by weight gain measurement (similar to EPA Reference Method 4) | -6.0 |
| Reactor Pressure Drop | Magnehelic differential pressure gauge | 4.5 |
| Reactor Inlet Temperature | Thermocouple with traverse of reactor inlet | 4.8 |
| Reactor Inlet $SO_2$ Concentration | EPA Reference Method 6 | -19.8 |

[1]Relative Error = $\dfrac{(\text{Process Measurement-Audit Result})}{\text{Audit Result}}$ X 100%

Overall, the QA audit test results show that the process measurements made by Chemico were accurate. However, an exception is the flue gas $SO_2$ concentration measurement by Chemico which was determined to be 20% low. This was due to the quenching effect of $O_2$ and $CO_2$ on the pulsed fluorescence monitor used to measure $SO_2$ concentration. This error is typical for this type of $SO_2$ instrument when calibrated with a reference gas of $SO_2$ in $N_2$, resulting in a lower $SO_2$ value when monitoring a gas stream containing oxygen and carbon dioxide. Studies have shown that this error can be as high as 30%. Chemico monitored the reactor inlet $SO_2$ concentration to determine the level of $SO_2$ to which the catalyst was exposed. Fortunately, this was not a critical measurement for characterizing the performance of the Hitachi-Zosen/Chemico pilot plant.

Based on the test results of Radian's QA audits, Chemico's process measurements were within the accuracy of the methods utilized. Therefore, there is no need to develop a correction factor for the process data. Chemico's process data can be used to characterize the performance of the pilot plant and serve as a basis for a technical evaluation of the HZ process.

## 4.4 CONTINUOUS $NO_x$ MONITOR CERTIFICATION TEST RESULTS

Certification tests of the continuous $NO_x$ monitors were conducted by Radian to ensure the accuracy of the $NO_x$ reduction data obtained by Chemico. The certification tests entail rigorous procedures to test monitors used at a commercial source for compliance with New Source Performance Standards. Because the HZ pilot plant was an experimental unit, some of the procedures were modified.

Table 4-5 lists the results of the continuous monitor certification tests for the $NO_x$ monitors at the HZ pilot plant. (More detailed results can be found in Appendix B).

TABLE 4-5.  CONTINUOUS $NO_x$ MONITOR CERTIFICATION TEST RESULTS AT HZ PILOT PLANT

| Certification Test | Performance Specification | HZ Pilot Plant | |
|---|---|---|---|
| | | Inlet $NO_x$ Monitor | Outlet $NO_x$ Monitor |
| Calibration Error | | | |
| -high level | ≤5% | 1.40 | 4.70 |
| -mid level | ≤5% | 4.39 | 2.68 |
| Response Time | ≤15 min | 1.4 | 1.6 |
| Zero drift (2-hour) | ≤2% | 1.20 | 0.05 |
| Calibration Drift (2-hour) | ≤2% | 1.93 | 1.78 |
| Relative Accuracy | ≤20%[1] | 14.1 | 10.5 |

[1]Alternatively, ≤10 percent of the applicable emissions standard.

The 24-hour zero and calibration tests were not performed as Chemico calibrated the $NO_x$ monitors every two hours; therefore, the 24-hour tests were irrelvant for these monitors.

The continuous monitor certification test results show that the continuous $NO_x$ monitors at the HZ pilot plant were functioning properly, so the data collected by Chemico accurately describes the pilot plant's $NO_x$ reduction performance.

## 4.5 STACK SAMPLING FOR SECONDARY EMISSIONS TEST RESULTS

A stack sampling program for secondary emissions was conducted by Radian to determine if any change in concentration occurred across the reactor. Table 4-6 summarizes the results of the secondary emissions sampling tests. The following discussion of the results describes their impact on commercial scale HZ process applications.

### Sulfur Trioxide

Sulfur trioxide ($SO_3$) samples were collected at the reactor inlet and outlet to determine if the HZ process produced $SO_3$ by the oxidation of $SO_2$. This was to be expected since the actual component of the HZ catalyst, vanadium pentoxide, is used commercially to catalyze $SO_2$ oxidation.

The results of each of the $SO_3$ tests are listed in Table 4-7. The test results indicate an average $SO_2$ oxidation of 1.5%. These results are in agreement with previous experience at SCR installations in Japan showing 1-2% $SO_2$ oxidation.

This increase in $SO_3$ concentration exiting the HZ reactor has potentially significant impacts on a commercial application of the HZ process. With over 50 ppm $NH_3$ exiting the reactor, the increased amount of $SO_3$ present will result in greater production of ammonium sulfates downstream, especially in the boiler air preheater. Ammonium sulfates can exist in the form of a liquid and/or solid solution. They are corrosive and can cause plugging of the preheater. The higher $SO_3$ concentration will also raise the initial formation temperature of the ammonium sulfates. This could necessitate the use of corrosion resistant material in the intermediate temperature zone of the preheater. Also, additional soot blowers may be needed along with increased soot blowing frequency.[3]

TABLE 4-6.  SUMMARY OF STACK SAMPLING TEST RESULTS AT HZ PILOT PLANT

| Flue Gas Component | Reactor Inlet Concentration[1] | Reactor Outlet Concentration[1] | Measurement Technique |
|---|---|---|---|
| Sulfur Trioxide | 8.4 ppmv (dry basis) | 20.7 ppmv (dry basis) | Controlled condensation, ion chromatograph |
| Particulate Loading | 7.1 gm/dscm | 7.7 gm/dscm | In stack filter |
| Hydrogen Cyanide[2] | <.01 mg/dscm | <.01 mg/dscm | Absorption, distillation, titration |
| Nitrosoamines[2] | <5 µg/dscm | <5 µg/dscm | Absorption, extraction, gas chromatograph w/nitrogen specific detector |
| Hydrocarbons[2] ($C_1$-$C_6$) | <1.0 ppmv | <1.0 ppmv | Gas chromatograph flame ionization detector |
| Carbon Monoxide[2] | <0.017% | <0.017% | Fischer gas partitioner |

[1]Average of 3 or more tests
[2]Below the detection limit

TABLE 4-7.   CHANGE IN $SO_3$ CONCENTRATION ACROSS THE REACTOR
AT THE HZ PILOT PLANT

| Test | $SO_3$ Inlet (ppm dry) | $SO_3$ Outlet (ppm dry) | $SO_2$ Oxidation (%) |
|------|------------------------|-------------------------|----------------------|
| 1    | 11.0                   | 25.3                    | 1.5                  |
| 2    | 7.5                    | 14.8                    | 1.1                  |
| 3    | 6.6                    | 21.9                    | 1.9                  |

### Particulate Matter (Fly Ash)

Particulate matter samples were collected from the HZ reactor inlet and outlet to quantify the fly ash loading to which the catalyst was exposed and to determine if catalyst erosion was occurring.

The results of the fly ash loading tests are shown in Table 4-8.

TABLE 4-8.   PARTICULATE MATTER LOADINGS MEASURED AT THE HZ PILOT PLANT

| Test | Inlet (gm/dscm) | Outlet (gm/dscm) |
|------|-----------------|------------------|
| 1    | 7.5             | 7.8              |
| 2    | 6.9             | 8.4              |
| 3    | 6.9             | -                |
| 4    | -               | 6.9              |

Particulate matter concentrations averaged 7.1 gm/dscm at the inlet and 7.7 gm/dscm at the outlet.  These results are quite consistent, especially considering that the sampling ports were located so that a traverse was possible in only one plane.

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Table 4-9 lists the results of the elemental analysis of the particulate matter samples taken at the HZ pilot plant. The elemental analysis test was performed to determine if there was an increase in titanium (Ti) or vanadium (V) concentration in the particulate matter exiting the reactor. The results show the concentrations of titanium and vanadium to be constant relative to the other elements, thus no measurable change in Ti or V concentration occurred. There is an apparent consistent increase in all the elements across the reactor. This was probably due to the presence of inert materials. Therefore, while catalyst erosion may have occurred, the rate of erosion produced no significant change in Ti or V concentration.

TABLE 4-9.  RESULTS OF PARTICULATE MATTER ELEMENTAL
ANALYSIS AT THE HZ PILOT PLANT[1]

| Component | Reactor Inlet | Reactor Outlet | Out/In |
|-----------|---------------|----------------|--------|
| Al | 10.7% | 13.0% | 1.21 |
| Ca | 8200 ppm | 9900 ppm | 1.21 |
| Fe | 4.9% | 6.0% | 1.22 |
| K | 2.0% | 2.5% | 1.25 |
| Mg | 6300 ppm | 7800 ppm | 1.24 |
| Mn | 190 ppm | 240 ppm | 1.26 |
| Sn | 490 ppm | 680 ppm | 1.40 |
| Na | 4200 ppm | 4700 ppm | 1.12 |
| Si | 18% | 23% | 1.28 |
| Zn | 190 ppm | 250 ppm | 1.32 |
| Cu | 150 ppm | 170 ppm | 1.13 |
| Ti | 5800 ppm | 6900 ppm | 1.19 |
| V | 270 ppm | 330 ppm | 1.22 |

[1]Concentrations are on a mass fraction basis

## Hydrogen Cyanide

Samples were collected and analyzed to determine if any HCN was being produced in the reactor by the reaction of $NH_3$ and hydrocarbons. Both reactor inlet and outlet samples were below the detection limit of the analytical method, 10 ppb. This is orders of magnitude less than the 10 ppm threshold limit value (TLV), maximum allowable for worker exposure. As a result, HCN production is not a problem with the HZ process.

## Nitrosoamines

Samples from the reactor inlet and outlet were collected and analyzed for nitrosoamine formation. Both samples were below the detection limit of the analytical procedure, $5\ \mu g/m^3$. This is well below the $65\ \mu g/m^3$ source concentration (for n-Nitrosodimethylamine which has the lowest safe level of aliphatic nitrosoamines) considered safe by EPA's multimedia environmental goals. This means that potential nitrosoamine production in the HZ reactor, if any, should not pose any environmental problems.

## Hydrocarbons (HC) and Carbon Monoxide (CO)

The concentration of both HC and CO at the reactor inlet and outlet were below the detection limit of the analytical method. No conclusion can be made about the impact of the HZ catalyst on these compounds, but it is unlikely that the HZ process produces them in significant amounts.

## Nitrous Oxide ($N_2O$)

$N_2O$ was excluded from the summary of results in Table 4-6 due to the analytical method used to measure $N_2O$ being unsuccessful. Several interfering peaks on the infrared (IR) spectrum along with the low level of any $N_2O$ present made detection impossible.

SECTION 5

EVALUATION OF THE HITACHI ZOSEN PROCESS


The overall objective of this study was to determine the technical and economic feasibility of applying the HZ process to a coal-fired utility boiler based on the results of the pilot plant tests. The approach used to meet this objective consisted of several elements. First, a basis was defined to permit preparation of a conceptual design and completion of material and energy balances for a specific application of the HZ process. The basis is a 500 MW coal-fired boiler and is identical to that used by TVA in preparing a preliminary economic analysis of several flue gas treatment processes including the HZ process.[2] The basis identified material flows to the process, the required reduction in $NO_x$ emissions, and the characteristics of unit operations not examined during the pilot plant tests. Using this information in conjunction with the pilot plant test results, a conceptual design was prepared.

Material and energy balances were completed for the process using the conceptual design results and process data which are representative of the pilot plant's operation. The results of the stack sampling tests conducted by Radian were also considered in preparing the material and energy balances. The results of this work identified the raw material and energy requirements of the process for the 500 MW application. Finally, a cost estimate was prepared for an HZ process applied to a 500 MW coal-fired boiler. This cost estimate used the estimate prepared by TVA as a basis. Equipment costs were adjusted for changes in process stream flowrates or other significant factors (e.g., changes in required catalyst volume). Using adjusted equipment costs and the calculated raw material and energy requirements, TVA's estimate was modified and a new cost estimate developed.

This section presents a discussion of the elements which comprised the evaluation of the HZ process. The basis for the evaluation is defined and the philosophy used in preparing the conceptual design is discussed. The conceptual design results are presented along with details and results of the material and energy balance calculations. The results of the cost estimate are also presented with details of how the estimate was prepared. Finally, a summary of results is presented with a discussion of how the results impact the technical and economic feasibility of the HZ process.

## 5.1 BASIS FOR THE EVALUATION OF THE HITACHI ZOSEN PROCESS

This evaluation of the HZ process consisted of examining the raw material and energy requirements and capital and annualized costs of the process for a specific application. This form was chosen for the evaluation to provide a basis for comparing the costs of the HZ process to the costs of other SCR processes which have been evaluated by TVA. In order to make these comparisons meaningful, it was necessary to use the same basis in this evaluation as was used by TVA in preparing their preliminary economic analysis. TVA's design basis is presented in detail in a report entitled "Preliminary Economic Analysis of $NO_x$ Flue Gas Treatment Processes" (EPA-600/8-80-021).[1] The following discussion summarizes the aspects of the design basis which are applicable to this evaluation of the HZ process.

### Power Plant Characteristics

Only one power plant was used in preparing the evaluation of the HZ process. This is a new, 500 MW coal-fired boiler, with an assumed Midwestern location for purposes of preparing cost estimates. The fuel for the plant was a coal having a heating value of 5820 kcal/kg and containing 3.5 percent sulfur and 16 percent ash. The coal composition and the input coal requirements (based on a heat rate of 2.27 Mcal/kWh) for the 500-MW boiler are listed in Table 5-1.

TABLE 5-1.  BASE CASE COAL COMPOSITION AND INPUT FLOW RATE
(500-MW new unit, 2.27 Mcal/kWh heat rate)

| Component | Wt %, as fired | kg/hr |
|---|---|---|
| C | 57.56 | 111,950 |
| $H_2$ | 4.14 | 8,030 |
| $N_2$ | 1.29 | 2,490 |
| $O_2$ | 7.00 | 13,610 |
| S | 3.12 | 6,080 |
| Cl | 0.15 | 270 |
| Ash | 16.00 | 31,120 |
| $H_2O$ | 10.74 | 20,870 |
| Total | 100.00 | 194,420 |

The composition of the flue gas at the exit of the economizer is that which will be processed by the HZ catalytic reactors since the temperature required in the reactor is close to the economizer exit temperature. This flue gas composition is presented in Table 5-2 and was estimated based on the assumption that 95 percent of the sulfur in the coal is emitted in the flue gas as $SO_x$ with 99 percent as $SO_2$ and 1 percent as $SO_3$. It is also assumed that 80 percent of the ash is emitted with the flue gas stream. The $NO_x$ concentration of the flue gas was estimates to be 640 ppm and consists of approximately 95 percent nitric oxide (NO) and 5 percent nitrogen dioxide ($NO_2$).

TABLE 5-2.  FLUE GAS COMPOSITION AND FLOW RATE AT THE ECONOMIZER OUTLET
(2.27 Mcal/kWh, 500-MW new unit, coal-fired, 3.5% S,
5820 kcal/kg HHV as fired, at 375°C)

| Component | Vol % | kg/hr |
|---|---|---|
| $N_2$ | 73.39 | 1,412,000 |
| $O_2$ | 3.23 | 71,000 |
| $CO_2$ | 13.56 | 410,100 |
| $SO_2$ | 0.26 | 11,400 |
| $SO_3$ | 0.003 | 144 |
| $NO_x$ | 0.064 | 1,365 |
| HCl | 0.012 | 300 |
| $H_2O$ | 9.48 | 117,300 |
| | 100.00 | 2,023,600 |

## Emission Reduction Requirements

The $NO_x$ reduction requirement for the HZ process in this evaluation is 90 percent. This level of $NO_x$ reduction was selected to determine the cost of achieving 90 percent $NO_x$ reduction using SCR. It should be noted that there are no federal regulations which require this level of $NO_x$ reduction.

## 5.2 CONCEPTUAL DESIGN OF THE HITACHI ZOSEN PROCESS FOR A 500 MW COAL-FIRED BOILER

The first step in the evaluation of the HZ process was to prepare a conceptual design for a 500 MW application of the process using the results of the pilot plant tests to define key process operating parameter and performance levels. In order to complete this step, it was necessary to evaluate and reduce the pilot plant test results to a form which would serve as a basis for the design. It was also necessary to make judgements concerning extrapolation of results from the pilot plant to a 500 MW scale.

With the pilot plant data in the appropriate form, it was then possible to define levels of key operating parameters such as the $NH_3/NO_x$ injection ratio, flue gas space velocity, reactor operating temperature, etc. It was also possible to determine the quantity of catalyst required to reduce $NO_x$ emissions by 90 percent for a 500 MW application. Once these items were defined, the conceptual design was essentially complete and material and energy balance calculations could be made based on the conceptual design results.

The following discussion presents the results of the conceptual design. It includes details of how the pilot plant test data were reduced and how those data were interpreted. It also includes a discussion of the general philosophy followed in preparing the design along with specific details of how the design was prepared.

## 5.2.1 Philosophy Used to Prepare the Conceptual Design

Chemico conducted a large number of tests with the HZ pilot plant. These tests were conducted under a variety of conditions using three separate charges of catalyst. For purposes of this evaluation it was necessary to determine how these test results would be interpreted to quantify process performance and, in fact, which test results would be used to prepare the conceptual design. The general philosophy followed in evaluating test data and in preparing the conceptual design for a 500 MW plant was to limit operating conditions to those which had been well documented in the pilot plant tests. In some cases it was necessary to extrapolate the test results, but this was minimized. The following discussion presents specific details of which tests were selected as a basis for this evaluation.

Several factors were considered in selecting the tests whose results would be used as a basis for this evaluation. First, it was considered desirable to have a large number of tests with repeatable results as a basis. The principal reason for this was that a greater number of tests allow a more accurate characterization of the process performance and more accurate estimates of process operating parameters such as reactor pressure drop, $NH_3/NO_x$ injection ratio, etc. Second, it was considered desirable to use tests with operating conditions similar to those in which Radian conducted the secondary emissions sampling program. For these reasons it was decided to use the results of the demonstration test conducted during the summer of 1980.

The demonstration test consisted of approximately 90 days of operation under essentially identical conditions. This provided an accurate characterization of key process operating parameters associated with specific levels of process performance. It was also during this test that Radian conducted the majority of the quality assurance and secondary emissions sampling tests so those results are directly applicable to a conceptual design based on the demonstration test.

As mentioned earlier, the general philosophy in preparing the conceptual design was to use the pilot plant data to the maximum extent and limit any extrapolation of results. More specifically, the design levels of key process operating parameters such as temperature and flowrate were based strictly on the levels measured during the demonstration test even though the optimization tests indicated it might be possible to improve process performance by changing some process operating parameters.

## 5.2.2 Pilot Plant Data Used to Prepare the Conceptual Design

The pilot plant data used to prepare the conceptual design were from the demonstration test. Because of the quantity of data collected during this test, it was possible to accurately characterize the average value of key process operating parameters. The repeatability of the test results is evidenced by the relatively small standard deviations of the key process operating parameters during the demonstration test (see Table 4-2).

The pilot plant data used in preparing the conceptual design are summarized in Table 5-3. The operating parameter levels shown represent averages of 7800 data points recorded during the demonstration test. One exception to this is the $NH_3$ emissions data which are the results of a relatively small number of manual sampling tests conducted by Chemico and Radian.

TABLE 5-3.  AVERAGE OPERATING PARAMETER LEVELS DURING THE 90-DAY
TEST OF THE HITACHI ZOSEN PILOT PLANT

| Operating Parameter | Average Value |
|---|---|
| Flue Gas Flowrate | 2200 $Nm^3/hr$ |
| $NH_3/NO_x$ Injection Ratio | 0.98 |
| Flue Gas Temperature | 370°C |
| Reactor Pressure Drop | 0.28 kPa |
| $NO_x$ Removal Efficiency | 89.8% |
| $NH_3$ Emissions | 54 ppmv |
| Inlet $NO_x$ Concentration | 451 ppmv |
| $SO_2$ Concentration | 1120 ppmv[1] |

[1]This concentration was adjusted based on the results of the QA audits.

## 5.2.3  Conceptual Design Constraints and Procedures

Once the pilot plant data to be used in the conceptual design had been selected, it was necessary to define design constraints and design procedures. The constraints used in preparing the conceptual design are summarized in Table 5-4.  The following discussion examines these constraints in detail along with the procedures used in preparing the conceptual design.

TABLE 5-4.  CONSTRAINTS FOR THE HITACHI ZOSEN CONCEPTUAL DESIGN

| Design Parameter | Level |
|---|---|
| Reactor Space Velocity | 8860 $hr^{-1}$ |
| $NH_3/NO_x$ Injection Ratio | 1.0 |
| $NH_3$ Emissions | .133 ppm/ppm $NO_x$ in |
| $SO_2$ Oxidation | 1.5% of inlet $SO_2$ |
| Reactor Operating Temperature | 340° to 410°C |

### Reactor Space Velocity

The reactor space velocity used in preparing the conceptual design is identical to the space velocity during the demonstration test.  Space velocity was determined by dividing the flue gas volumetric flowrate (5200 $m^3$/hr) by the catalyst volume (0.587 $m^3$).  Scale-up of the reactor is straightforward.  One stack of catalyst 0.276 $m^2$ x 2.13 m is required for each 5200 $m^3$/hr of flue gas. It is necessary for the space velocity and the catalyst configuration to be constant for both the pilot unit and the conceptual design.  This permits direct use of other test data in preparing the conceptual design.

It should be noted that the space velocity specified for the conceptual design is a maximum and thus applies to the flue gas flowrate from the boiler at full load.  As discussed in Section 4, reduced space velocities (at reduced loads) should not change the $NO_x$ reduction efficiency of the reactor.

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## NH₃/NO$_x$ Injection Ratio

The NH$_3$/NO$_x$ injection ratio during the HZ pilot demonstration test averaged 0.98 while the NO$_x$ reduction efficiency averaged 89.8 percent. Since the conceptual design requires 90 percent NO$_x$ reduction, a slightly higher NH$_3$/NO$_x$ injection ratio is needed. Examination of the data presented in Figure 4-2 shows that the HZ process NO$_x$ reduction efficiency should be 90 percent at an NH$_3$/NO$_x$ injection ratio of 1.0. This is the level selected for the conceptual design.

## NH₃ Emissions

NH$_3$ emissions from the HZ process are important from several standpoints. First and most important, the level of NH$_3$ emissions determines the severity of impacts on downstream equipment. NH$_3$ emitted from an SCR reactor can result in plugging and corrosion of the air preheater, which can increase the costs associated with the application of SCR. The level of NH$_3$ emissions can also determine the extent of adverse environmental impacts (if any) from the SCR process. Previous work has shown that excessive NH$_3$ emissions can result in environmental problems.

The NH$_3$ emissions for the conceptual design were estimated to be .133 ppm NH$_3$ per ppm NO$_x$ in. This estimate is based on an analysis of NH$_3$ emissions as a function of NO$_x$ inlet and the NH$_3$/NO$_x$ injection ratio (Figure 4-6). For the conceptual design with an inlet NO$_x$ concentration of 640 ppm, this results in an NH$_3$ concentration at the reactor oulet of 85 ppmv.

## SO₂ Oxidation

SO$_2$ oxidation was measured during the demonstration test as part of the secondary emissions sampling program conducted by Radian. Based on Radian's measurements SO$_2$ oxidation averaged 1.5 percent of the SO$_2$ in the flue gas. Since the conceptual design has operating characteristics identical to the HZ pilot unit, the fraction of SO$_2$ oxidized is also expected to be identical.

For the conceptual design which has a flue gas $SO_2$ concentration of 2590 ppm, this results in an additional 39 ppm of $SO_3$ in the flue gas at the reactor exit.

$SO_2$ oxidation is important due to its potential impacts on downstream equipment. By itself, $SO_3$ can cause severe corrosion in the extreme cold end of the air preheater or in downstream duct work and equipment such as an ESP. And when $NH_3$ is present in the flue gas, additional $SO_3$ can result in the formation of liquid ammonium bisulfate in the intermediate temperature zone of the air preheater which, for typical air preheater designs, is more susceptible to corrosion and plugging. Thus the additional $SO_3$ in the presence of $NH_3$ can cause severe operating problems in the air preheater.

### Reactor Operating Temperature

The reactor operating temperatures specified for the conceptual design ranges from 340 to 410°C even though the operating temperature during the demonstration test was maintained at 370°C. The range specified is based on the results of the optimization tests which show little effect of operating temperature on $NO_x$ reduction efficiency in this reactor. Since the reactor can operate over a range of temperatures without impacting $NO_x$ reduction, the conceptual design does not include requirements for flue gas temperature control at the reactor inlet.

### 5.2.4 Conceptual Design Results

The preceding discussion has summarized the data used and the limitations observed in preparing the conceptual design of a 500 MW HZ process. The discussion which follows summarizes the results of the design calculations and examines results in detail.

Table 5-5 summarizes the results of the conceptual design calculations. As shown, key design variable levels are presented for the SCR reactor and the downstream air preheater. The design levels presented for the reactor are

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based on the information outlined in the preceding discussion and the basis defined in Section 5.1, while the air preheater design parameters are based on the results of a study on ammonium sulfate formation in air preheaters.[3] Design parameters for the air preheater are presented because the reactor design results in high concentration of both $NH_3$ and $SO_3$ at the reactor outlet. For a conventional air preheater design, the expected $NH_3$ and $SO_3$ concentrations at the reactor outlet cause severe corrosion and plugging problems. As a result, modification of the air preheater design is required to minimize those problems. The following discussion examines the reactor and air preheater design parameter levels specified in the conceptual design.

## Reactor Design Parameters

The basis for the reactor design has been outlined in this Section. The number of reactors was selected to be identical to the design used in TVA's preliminary economic analysis of flue gas treatment processes. Reactor cross-section was determined by dividing the flue gas flowrate for the 500 MW plant by the flowrate to the pilot unit and multiplying by the crossectional area of the pilot plant reactor. Catalyst volume was obtained by multiplying the crossectional area by the catalyst depth of the pilot unit (2.0 m).

Reactor pressure drop was 0.28 kPa during the pilot scale tests and was assumed to be identical for the 500 MW design. An additional 1.0 kPa pressure drop was assumed for ducts and flow distributors in the full scale design. Only a single soot blower was used on the pilot plant while four soot blowers were included in the conceptual design. The additional soot blowers were included in the conceptual design to reflect current practice in Japan where a soot blower is placed between each layer of catalyst. (The pilot plant and the conceptual design both have four layers of catalyst blocks with each block 0.5 m on a side). The soot blowing frequency specified for the conceptual design is 3 times per day and this reflects actual operating experience at the HZ pilot plant.

## Air Preheater Design Parameters

The expected concentration of $NH_3$ and $SO_3$ at the reactor outlet are 85 ppm and 65 ppm respectively. An investigation of ammonium sulfates formation in air preheaters has shown that these concentrations will result in severe corrosion and plugging of the preheater. This results in the requirement for corrective measures to minimize problems in the air preheater. The same investigation of air preheater problems concluded that the optimum solution to the problem is to employ available air preheater design options designed to minimize corrosion and plugging. These air preheater design options were presented in Table 5-5.

TABLE 5-5. RESULTS OF THE CONCEPTUAL DESIGN FOR A 500 MW. HITACHI ZOSEN PROCESS

| Design Parameter | Design Level |
|---|---|
| **Reactor Design Parameters** | |
| • Number of Reactors | 2 |
| • Reactor Crossection ($m^2$) | 96.5 |
| • Catalyst Volume per reactor ($m^3$) | 205 |
| • Reactor System Pressure Drop (kPa) | 1.28 |
| • Soot Blowers per Reactor | 4 |
| • Soot Blowing Frequency | 3/day |
| **Air Preheater Design Parameters** | |
| • Soot Blowers per Preheater | 6 |
| • Soot Blowing Frequency | 6/day |
| • Element Configuration | Combined Intermediate and Low Temperature Zone |
| • Element Construction | Corrosion Resistant Material in Intermediate-Low Temp Zone |

Use of additional soot blowers and increased soot blowing frequency is intended to aid in cleaning deposits from the preheater. The combined heat transfer elements are also designed to aid in cleaning deposits from the preheater by making the soot blower more effective in the intermediate zone of the preheater where ammonium sulfates tend to form. Corrosion resistant material is used to minimize corrosion due to the formation of liquid ammonium bisulfate, the product expected downstream of the 500 MW application of the HZ process.

It should be noted that these air preheater design options impact the cost estimate for the HZ process and are included in the costs presented later in this section. However, it should also be noted that these costs may not adequately reflect the costs which will result from the high $NH_3$ and $SO_3$ emissions estimated for the HZ process. The emission rates estimated for the conceptual design are much higher than any considered in the study of air preheater problems, and therefore the use of available air preheater design options may not solve the problems of ammonium sulfate plugging and corrosion.

## 5.3 MATERIAL BALANCE FOR A 500 MW HITACHI ZOSEN PROCESS

The first step in completing the HZ process evaluation was preparation of a conceptual design. Once this design was completed it was then possible to complete material balance calculations which define raw material requirements for a 500 MW HZ system. This was done using TVA's material balance as a basis and the data generated during the pilot plant tests and secondary emissions sampling to modify that material balance. Where appropriate, ratios of modified stream flows to TVA's original flows were made to determine new flowrates (e.g., the quantity of air used to dilute/inject $NH_3$).

Figure 5-1 is a schematic of the HZ process which indicates process streams and stream numbers considered in preparing the material balance. This schematic and the stream numbers shown are consistent with those used by TVA.
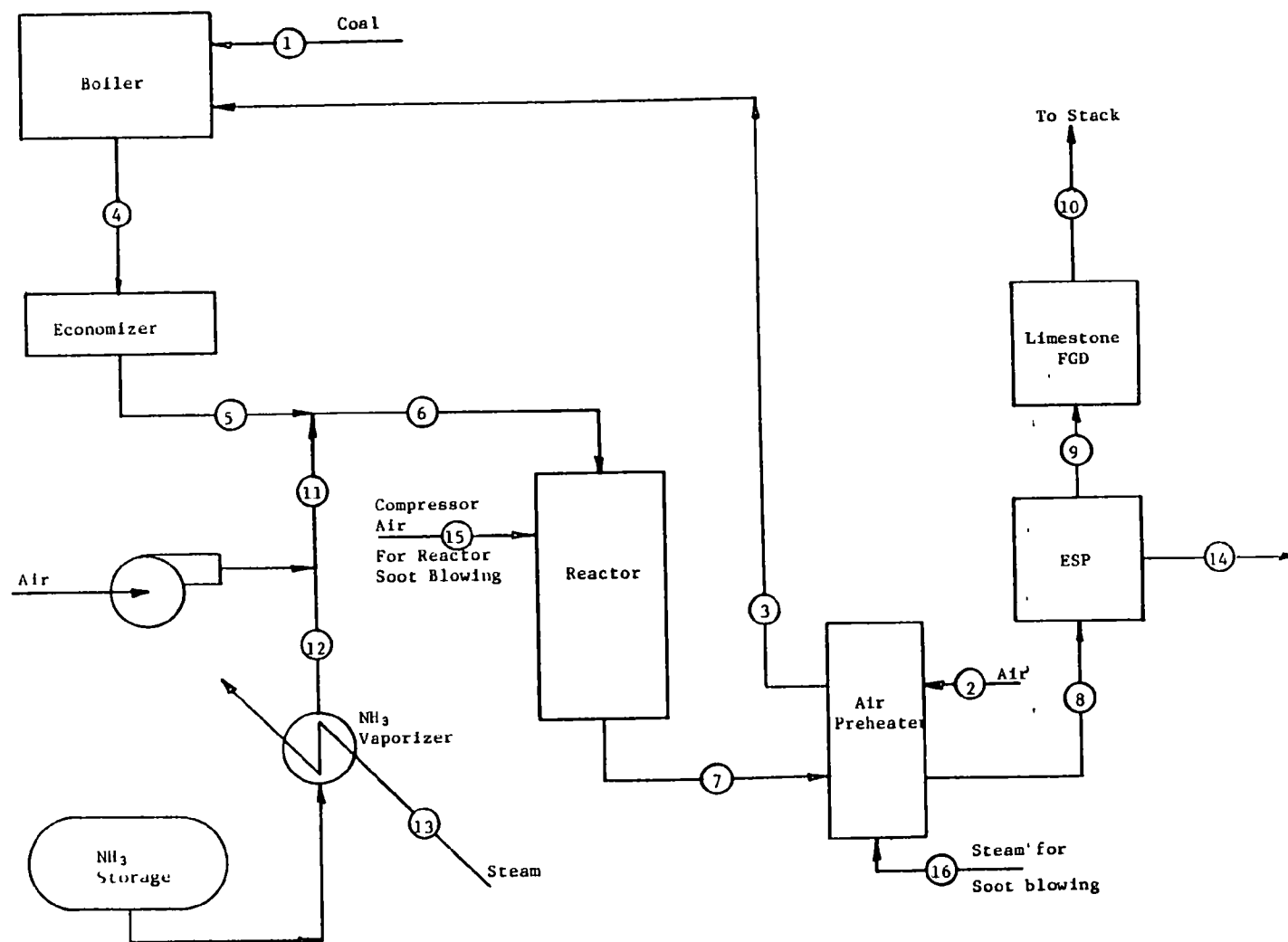
Figure 5-1. Hitachi Zosen process flowsheet.

There are, however, two additional streams shown in Figure 5-1. These represent the compressed air used for soot blowing the reactor (stream 15) and the additional steam required for soot blowing the modified air preheater (stream 16).

The results of the material balance calculations based on the pilot plant data are summarized in Table 5-6. These represent the mass and volumetric flows to all significant pieces of process equipment in the 500 MW application of the HZ process. These flowrates were estimated based on the data and assumptions outlined in the preceding discussion. The results of the material balance calculations serve as a basis for the energy balance calculations which are summarized in the following section. These flows also serve as a basis for estimating the size and consequent cost of process equipment for the 500 MW application of the HZ process.

In comparing the results of the material balance calculations presented in Table 5-6 with those developed by TVA, there are no major differences in material flowrates. The most significant difference is the estimated $NH_3$ and $SO_3$ emissions from the HZ reactor and the consequent requirement for additional soot blowing of the air preheater. The only other difference is the requirement for compressed air for reactor soot blowing. TVA's design did not include reactor soot blowing, but it was included in this evaluation since soot blowing was a routine part of the pilot plant's operation. These differences and the requirement for air preheater modifications result in a slight increase in HZ process costs which are discussed in Section 5.5.

## 5.4  ENERGY REQUIREMENTS FOR A 500 MW HITACHI ZOSEN PROCESS

The material balance presented the mass flowrates of various process streams in the HZ process. With this as a basis, it was possible to complete an energy balance and to determine the energy requirements for a 500 MW application of the process. Determination of the energy requirements involved consideration of several factors including:

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TABLE 5-6. MATERIAL BALANCE FOR 500 MW HITACHI ZOSEN PROCESS*

| Stream Number | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| Description | Coal to Boiler | Combustion Air to Air Heater | Combustion Air to Boiler | Flue Gas to Economizer |
| Mass Flow (lb/hr) | 428,600 | 4,546,200 | 4,101,800 | 4,516,100 |
| Volume Flow (scfm) | · | 1,005,000 | 906,700 | 957,000 |

| Stream Number | 5 | 6 | 7 | 8 |
|---|---|---|---|---|
| Description | Flue Gas to Reactor | Flue Gas – $NH_3$ Mixture to Reactor | Flue Gas to Air Heater | Flue Gas to ESP |
| Mass Flow (lb/hr) | 4,516,100 | 4,570,800 | 4,570,800 | 5,015,200 |
| Volume Flow (scfm) | 957,000 | 969,200 | 969,200 | 1,066,700 |

| Stream Number | 9 | 10 | 11 | 12 |
|---|---|---|---|---|
| Description | Gas to FGD Unit | Treated Flue Gas to Stack | $NH_3$ Air Mixture Injected Into Flue Gas | $NH_3$ From Storage |
| Mass Flow (lb/hr) | 4,960,700 | 5,160,000 | 54,700 | 1,650 |
| Volume Flow (scfm) | 1,066,700 | 1,139,900 | 12,200 | – |

| Stream Number | 13 | 14 | 15 | 16 |
|---|---|---|---|---|
| Description | Steam to $NH_3$ Vaporizer | Fly Ash from ESP | Compressed Air for Reactor Soot Blowing | Steam for Air Heater Soot Blowing |
| Mass Flow (lb/hr) | 1,011 | 54,600 | 2,530 | 7,700 |
| Volume Flow (scfm) | 355 | – | 555 | 2,700 |

*Note: For ease of comparison with TVA's results, the values in this table are presented in English units.

- Evaluation of any heat credits associated with the
  HZ process,

- Determining the enthalpy of all streams entering and
  exiting the process; and

- Determining the electrical energy required for fans and
  compressors.

Once each of these factors had been evaluated it was possible to determine
the overall energy demands of the HZ process.

The following discussion examines each of the above factors in detail
and summarizes the estimated energy requirements of the HZ process.

## 5.4.1 Hitachi Zosen Process Heat Credits

Because the HZ process is located between the economizer and air pre-
heater of a boiler, the potential exists to recover heat added to the flue
gas by the process. In the HZ process, the $NO_x$ reduction reactions and the
$NH_3$ oxidation reaction are exothermic and so it is possible to recover the
heat of these reactions in the air preheater. Table 5-7 presents the reactions
which can occur in an HZ reactor. This table also identifies the heats of
reaction and, based on material balance calculations, the quantity of heat
which is added to the flue gas due to these reactions. As shown, no heat is
added to the flue gas as a result of $NH_3$ oxidation. This is due to the fact
that, within the accuracy of the process measurements, the pilot plant test
results indicated that no $NH_3$ oxidation occurred in the reactor.

TABLE 5-7.  REACTIONS WHICH CAN ADD HEAT TO FLUE GAS
IN THE HITACHI ZOSEN PROCESS

| Reaction | $\Delta H_{400°C}$ | Heat Added to Flue Gas (Gcal/hr) |
|---|---|---|
| $4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$ | -96.98 kcal/gmol $NH_3$ | 3.68 |
| $4NO_2 + 4NH_3 + O_2 \rightarrow 3N_2 + 6H_2O$ | -39.34 kcal/gmol $NH_3$ | 0.16 |
| $4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O$ | -75.3 kcal/gmol $NH_3$ | $\sim 0$ |

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The heat of the $NO_x$ reduction reactions results in about a 7°C temperature rise across the HZ reactor. This heat credit is offset to some extent by a heat debit which results from the assumption that the $NH_3$-air mixture is injected into the flue gas at 38°C. This heat debit is estimated to be approximately 0.7 Gcal/hr so the net heat credit for the HZ process is 3.15 Gcal/hr.

## 5.4.2 Energy Balance for the 500 MW Hitachi Zosen Process

Once the HZ heat credits were evaluated it was possible to use that information in conjunction with the results of the material balance to complete an energy balance for the HZ process. This energy balance considered all the major streams entering and exiting the process. In addition, the heat credit discussed in the preceding section was included. It should be noted that the energy balance does not represent a comprehensive evaluation of the energy requirements of the process since it does not include electrical energy requirements. This is considered later in this section.

The results of the energy balance calculations for the 500 MW application of the HZ process are summarized in Table 5-8. The energy associated with major inputs and outputs are shown for major process streams. These energy balance results include the heat credits and energy debit discussed in the preceding section.

TABLE 5-8. SUMMARY OF ENERGY BALANCE CALCULATIONS FOR
500 MW APPLICATION OF THE HZ PROCESS

| Stream Description | Enthalpy (Gcal/hr) |
|---|---|
| Gas Streams to Process | |
| Flue Gas to Blower | 191.50 |
| $NH_3$-Air Mixture | 0.23 |
| Combustion Air to Air Heater | 13.75 |
| Gas Streams from Process | |
| Flue Gas to ESP | 84.68 |
| Combustion Air to Boiler | 133.13 |
| Steam to Process | |
| Additional Steam for Air Preheater Soot Blowing | 2.90 |
| Steam to $NH_3$ Vaporizer | 0.30 |

Electrical Energy Requirements of the 500 MW HZ Process

The component of the overall energy requirements of the HZ process which had not yet been defined is the electrical energy requirement. Electrical energy is required by the process to operate fans and compressors. In conjunction with process steam requirements and the net process heat credit, the electrical energy requirements can be used to define the overall energy requirement for the 500 MW application of the HZ process.

Electrical energy requirements were estimated for the fans and compressors used in the HZ process. This estimate was prepared by determining the theoretical work required by each item of equipment and assuming an efficiency of 70 percent for conversion of electrical energy to mechanical work.

The estimated electrical energy requirements for a 500 MW application of the HZ process are summarized in Table 5-9. As shown, the single largest energy requirement is that associated with the main flue gas blower. This accounts for nearly 90 percent of the total electrical energy. It should be noted that the flue gas fan energy requirement represents only the incremental power required to overcome the pressure drop associated with the SCR system.

TABLE 5-9.  ESTIMATED ELECTRICAL ENERGY REQUIREMENTS FOR A
500 MW APPLICATION OF THE HITACHI ZOSEN PROCESS

| Process Equipment Item | Theoretical Energy Requirement (kW) | Estimated Actual Energy Requirement (kW) |
|---|---|---|
| $NH_3$ Compressor | 84 | 120 |
| Reactor Soot Blower Compressor[1] | 49 | 70 |
| $NH_3$ Injection Blower | 7 | 10 |
| Flue Gas Blower[2] | 939 | 1341 |
| Total | 1079 | 1541 |

[1]This represents average energy demand. The energy requirement is much greater during soot blowing of the reactor.

[2]This represents incremental power required by the flue gas blower.

## 5.4.4 Overall Energy Requirements for the 500 MW Application of the Hitachi Zosen Process

The preceding discussion has defined the basis for and presented the results of calculations which estimate the individual components of the energy requirements for a 500 MW application of the HZ process. This section summarizes these results and puts the individual components of the process energy requirements on a common basis.

Table 5-10 presents the individual components and the estimated overall energy requirements for a 500 MW application of the HZ process. Each of these components has been put on the basis of heat input to the boiler. For steam, a thermal efficiency of 88 percent was used to determine the energy input required to generate one Gcal of steam energy. For electricity, a boiler heat rate of 2.27 Mcal/kWh was used. The heat credit was assumed to replace heat input to the boiler on a 1-to-1 basis.

As shown in Table 5-10, the overall energy requirement for the 500 MW application of the HZ process is about 4.0 Gcal/hr which represents only 0.33 percent of the boiler's capacity. Both the steam and electrical energy requirements are similar and the heat credit results in about a 50 percent reduction in process energy requirements.

TABLE 5-10. OVERALL ENERGY REQUIREMENT FOR A 500 MW
APPLICATION OF THE HZ PROCESS

| Energy Area | Energy Requirement (Gcal/hr) | Percent of Boiler Capacity |
|---|---|---|
| Heat Credit | (3.15) | (0.28) |
| Steam | 3.36 | 0.30 |
| Electricity | 3.50 | 0.31 |
| Total | 3.99 | 0.33 |

## 5.5 ESTIMATED COSTS FOR A 500 MW APPLICATION OF THE HITACHI ZOSEN PROCESS

The final step in the evaluation of the HZ process was to prepare a modified cost estimate for a 500 MW application of the process. This cost estimate includes an estimate of both capital costs and annual revenue requirements. It was prepared to show how the results of the pilot plant tests affected the economics of the process. Because the estimate used the same basis as TVA's preliminary economic analysis, the results can be used to compare HZ process costs with the costs of other SCR processes. It should be noted, however, that the comparison is only for a specific application of the HZ process and the results may not be valid for other applications.

The procedure used in preparing the estimate of capital costs and annual revenue requirements was to first define equipment costs for the process. This was done using TVA's original equipment cost list and standard exponential capacity factors for chemical process equipment. Installation costs for piping, insulation, foundations, etc. were estimated as a percentage of the equipment costs. Once the installed equipment costs were defined, the total capital costs and annual revenue requirements were estimated. The estimates of these costs used factors developed by TVA along with the results of the conceptual design and material and energy balances developed as part of this study.

An additional item included in the cost estimate was the cost of air preheater modifications needed to minimize the impact of $NH_3$ and $SO_3$ emissions from the process. These costs were taken from a study conducted by Radian Corporation entitled "Ammonium Sulfate and Bisulfate Formation in Air Preheaters". These costs were based on a quote supplied by C-E Air Preheater.

The following discussion presents the results of the estimates of capital costs and annual revenue requirements for the HZ process. It includes a brief discussion of how the estimates were derived and a comparison of the modified

HZ cost estimate with the costs of other SCR processes as determined by TVA. A detailed discussion of the economic premises used to prepare the cost estimates along with an estimate of individual equipment item costs is presented in Appendix D of this report.

## 5.5.1 Estimated Total Capital Investment for a 500 MW Application of the HZ Process

### Procedure for Estimating Capital Investment

The capital cost estimate for the HZ process was based primarily on the costs of process equipment. These costs were estimated for individual items of process equipment using the equipment costs developed by TVA and Radian as a basis. Modified equipment costs were determined by comparing process flowrates for individual equipment items and using cost-size exponents which reflect equipment cost-size relationships typical of the chemical process industry. In the case of the catalyst, it was assumed that the cost of the NOXNON 600 catalyst is equal to that of the NOXNON 500 on a volume basis. It was also assumed that no economy of scale was realized for the catalyst (i.e., the cost per unit volume of catalyst is constant). Using this procedure, the costs for individual equipment items were determined. These costs should accurately reflect modified costs since, in nearly all cases, the size did not vary significantly from the equipment sizes in the original cost estimate. These costs are representative of a Midwestern power plant location and mid-1979 dollars. The costs were not escalated to 1981 dollars in order to facilitate comparison with estimated costs for other SCR processes.

Once equipment costs were determined, the various installation expenses such as piping, foundations, etc., were estimated as a percentage of equipment costs. The sum of the process equipment costs and installation expenses constituted the major components of the direct investment. The final component

of the total direct investment includes a services and miscellaneous cost which was calculated as a percentage of the installed equipment cost. The sum of the installed equipment cost and the services and miscellaneous cost is the total direct investment.

The total indirect investment (the sum of various indirect investments, such as engineering design and supervision, A&E contractor, construction expense, and contractor fees) was calculated based on the total direct investment using formulas described in Appendix D of this report. A contingency, calculated as 20% of the sum of the total direct and total indirect investment, was also included. The sum of the total direct investment, the total indirect investment, and the contingency equals the total fixed investment.

Other capital charges included in the cost estimates consist of an allowance for startup and modification, interest during construction, land costs, working capital. The allowance for startup and modification and interest during construction were calculated as a percentage of the total fixedinvestment, the previously calculated allowance for startup and modification, and interest during construction. The sum of total depreciable investment, land costs, and working capital is the total capital investment.

## Results of Capital Cost Estimate

Table 5-11 presents the individual components and the estimated total capital investment for a 500 MW application of the HZ process. As shown, the total capital investment was estimated to be approximately $22.1 x 10^6$ which is equivalent to \$44/kW of generating capacity. This compares to TVA's previous estimate of $23.3 x 10^6$ and it represents a slight decrease in totalcapital investment. The principal difference between the two estimates is the lower catalyst volume required for the design based on the pilot plant results. This lower catalyst volume is a result of the greater space velocities in the pilot

TABLE 5-11. ESTIMATED CAPITAL INVESTMENT FOR A 500 MW APPLICATION
OF THE HITACHI ZOSEN PROCESS[a]

| | Investment, $ | % of total direct investment |
|---|---|---|
| Direct Investment[b] | | |
| NH₃ storage and injection | 645,000 | 5.5 |
| Reactor section | 8,632,000 | 73.4 |
| Gas handling | 351,000 | 3.0 |
| Air preheater modifications | 1,461,000 | 12.4 |
| Sub-total direct investment (DI) | 11,089,000 | 94.3 |
| Services, utilities (0.06 x DI) | 665,000 | 5.7 |
| Total direct investment (TDI) | 11,754,000 | 100.0 |
| | | |
| Indirect Investment | | |
| Engineering design and supervision | 274,000 | 2.3 |
| Architect and engineering contractor | 69,000 | 0.6 |
| Construction expense = 0.25 (TDI x 10⁻⁶)^0.83 | 1,933,000 | 16.4 |
| Contractor fees = 0.096 (TDI x 10⁻⁶)^0.76 | 625,000 | 5.3 |
| Total indirect investment (IDI) | 2,901,000 | 24.7 |
| Contingency = 0.2 (TDI + IDI) | 2,931,000 | 24.9 |
| Total fixed investment (TFI) | 17,586,000 | 149.6 |
| | | |
| Other Capital Charges | | |
| Allowance for startup and modifications = (0.1) (TFI) | 1,759,000 | 15.0 |
| Interest during construction = (0.12) (TFI) | 2,110,000 | 17.9 |
| Total depreciable investment | 21,455,000 | 182.5 |
| Land | 5,000 | - |
| Working capital | 336,000 | 2.9 |
| Royalty fee | 300,000 | 2.6 |
| TOTAL CAPITAL INVESTMENT | 22,096,000 | 188.0 |

[a] Basis: 500 MW new coal-fired power plant, 3.5% sulfur coal, 90% NOx removal.
Midwest plant location. Represents project beginning mid-1977, ending mid-1980.
Average basis for scaling, mid-1979. Investment requirements for fly ash
disposal excluded. Construction labor shortages with overtime pay incentive
not considered.

[b] Each item of direct investment includes total equipment costs plus installation
labor, and material costs for electrical, piping, ductwork, foundations,
structural, instrumentation, insulation, and site preparation.

plant tests compared to those used by TVA in preparing the preliminary cost estimate. To some extent, the lower costs of catalyst are offset by the capital costs for the air preheater modifications. The net effect is that essentially no change in the process capital costs is expected based on the pilot plant test results.

## 5.5.2 Estimated Average Annual Revenue Requirements for a 500 MW Application of the HZ Process

### Procedure for Estimating Annual Revenue Requirements

The annual revenue requirements were calculated based on a Midwestern power plant location and mid-1980 costs. These average annual revenue requirements were divided into the direct costs, which consists of raw materials costs and conversion costs, and indirect costs, which consist of capital charges and overheads.

In calculating direct costs, the raw material, utility, and labor unit costs used were those developed by TVA while the required quantities of these cost items were based on the conceptual design and the material and energy balance results. The maintenance cost was calculated as a percentage of total direct investment.

The capital charges portion of the indirect costs consists of: (1) depreciation, interim replacements, and insurance, which were estimated based on the total depreciable investment; and (2) the average costs of capital and taxes, which were determined based on the total capital investment. The overhead charges consist of: (1) plant overhead, which was estimated as a percentage of the cost of operating labor and supervision, maintenance, and analyses; and (2) administrative overheads, which were estimated based on a

percentage of operating labor and supervision. Specific details of how each of the components of the annual revenue requirements was estimated are pre-sented in Appendix D.

The annual revenue-requirements were determined as the sum of the direct and the indirect costs. Equivalent unit revenue requirements in mills/kWh were then obtained by dividing by the on-stream time of 7000 hr/yr and the plant MW rating.

## Results of the Annual Revenue Requirement Estimate

Table 5-12 presents the individual components and the total estimated average annual revenue requirements for a 500 MW application of the HZ process. As shown, the average annual revenue requirement was estimated to be approximately $10.3 x 10^6$/yr which is equivalent to 2.91 mills/kWh. This compares to TVA's previous estimate of $12.2 x 10^6$/yr and represents nearly a 16 percent decrease in the annual revenue requirements for the process.

As with the capital costs, the principal factor which changed the annual revenue requirements is the decreased quantity of catalyst required in the reactor. Again, the lower catalyst requirements are partially offset by the increased costs associated with the air preheater modifications (i.e., in-creased soot blowing).

## 5.5.3 A Comparison of Capital Investment and Annual Revenue Requirements of the HZ Process with the SFGT Process

The capital investment and annual revenue requirements of the HZ process have been estimated based on the results of the test conducted at the EPA sponsored pilot unit in Albany, Georgia. The results of these cost estimates indicate that the capital costs and annual revenue requirements are slightly lower than the estimated costs prior to the test program. A more significant indication of how the pilot plant results affect HZ process costs is a comparison of HZ process costs to the costs of the other SCR process tested during the EPA $NO_x$ pilot plant program, the shell flue gas treating (SFGT) process.

TABLE 5-12. ESTIMATED AVERAGE ANNUAL REVENUE REQUIREMENTS FOR A 500 MW APPLICATION OF THE HITACHI ZOSEN PROCESS[a]

| Item | Annual quantity | Unit cost($) | Annual cost($) | % of annual revenue required |
|---|---|---|---|---|
| **Direct Costs** | | | | |
| Raw materials | | | | |
| $NH_3$ | $5.25 \times 10^6$ kg | 0.165/kg | 866,300 | 8.47 |
| Catalyst | | | 5,125,000 | 50 14 |
| Total raw materials | | | 5,991,300 | 58 51 |
| Conversion costs | | | | |
| Operating labor and supervision | 8760 labor hrs. | 12.50/ labor hr. | 109,500 | 1 07 |
| Utilities | | | | |
| Steam | 20,700 Gcal | 7.94/Gcal | 164,400 | 1.61 |
| Electricity | 10,787,000 kWh | 0.029/kWh | 312,800 | 3.06 |
| Heat credit | 22,050 Gcal | -7.94/Gcal | (175,100) | (1.71) |
| Maintenance = .04 x TDI | | | 470,200 | 4.60 |
| Analyses | 2,920 labor hrs. | 17.00/ labor hr. | 49,600 | 0 48 |
| Total conversion costs | | | 931,400 | 9 11 |
| Total direct costs | | | 6,922,700 | 67.72 |
| **Indirect Costs** | | | | |
| Capital charges | | | | |
| Depreciation = (0.06) (total depreciable investment) | | | 1,287,300 | 12.59 |
| Average cost of capital = (0.086) x (total capital investment) | | | 1,900,300 | 18.59 |
| Overheads | | | | |
| Plant = (0.5) (conversion costs minus utilities) | | | 314,700 | 3.08 |
| Administrative = (0.1) (operating labor costs) | | | 11,000 | 0.11 |
| Total indirect costs | | | 3,513,300 | 34.37 |
| Spent catalyst disposal | | | (214,000) | (2 09) |
| TOTAL ANNUAL REVENUE REQUIREMENTS | | | 10,222,000 | 100 00 |

[a] Basis: 500 MW new coal-fired power plant, 3.5% S coal. 90 percent $NO_x$ reduction, 90 percent $SO_2$ removal. Midwest power plant location, 1980 revenue requirements. Remaining life of power plant = 30 years. Plant on line 7000 hr/yr. Plant heat rate equals 9.5 MJ/kWh. Investment and revenue requirement for disposal of fly ash excluded. Total direct investment $11,754,000; total depreciable investment $21,455,000, and total capital investment $22,096,000.

Since the same basis was used in preparing the modified HZ cost estimate as TVA used in preparing preliminary economic estimates for other SCR processes, it is possible to make a direct comparison using TVA's previously published results to account for process differences. Table 5-13 shows the estimated capital investment for two pollution control systems which reduce emissions of particulates, $NO_x$, and $SO_x$ by 99.5, 90, and 90 percent respectively. As shown, the three pollution control systems employ two different SCR process, one being the HZ process and the other, the SFGT process which also removes $SO_2$ from the gas. The HZ process cost is added to the cost of a flue gas desulfurization system and both SCR systems include ESP's located downstream in order to put the cost estimates on a common basis.

TABLE 5-13. ESTIMATED CAPITAL INVESTMENT FOR THREE POLLUTION CONTROL SYSTEMS[1]

| SCR Process | Total Capital Investment ($ x $10^{-6}$) | | | |
|---|---|---|---|---|
| | SCR | FGD | ESP | Overall |
| Shell Flue Gas Treatment | 84.2 | – | 14.6 | 98.8 |
| Hitachi Zosen | 22.1 | 50.4 | 10.8 | 83.3 |

[1]All costs except the HZ-SCR and the Shell Flue Gas Treatment (SFGT)-SCR cost are from "Preliminary Economic Analysis of $NO_x$ Flue Gas Treatment Processes". Tennessee Valley Authority - Office of Power, EPA - 600/7-80-021, February, 1980. Costs for the SFGT-SCR estimated in "Independent Evaluation of the Shell Flue Gas Process", Radian Corporation - Draft Final Report. EPA Contract No. 68-02-3171, Task 11.

As shown on Table 5-13, the HZ process requires lower capital investment, having a capital cost nearly 20 percent lower than the SFGT process. This indicates that the HZ process represents the more economic SCR system for this particular 500 MW application within the accuracy of the cost estimates.

Table 5-14 presents the annual revenue requirements for the two pollution control systems. As shown, the estimated costs associated with the HZ processes are 30 percent lower than those of the SFGT process. The results presented in Table 5-14 indicate that the HZ process, as tested in the pilot plant and presented in the conceptual design, is more economical than the SFGT process for the 500 MW application examined in this study. It should be noted that the relative costs presented in Table 5-14 are only valid for one specific application and they could change for other applications.

TABLE 5-14. ESTIMATED ANNUAL REVENUE REQUIREMENTS FOR THREE POLLUTION CONTROL SYSTEMS[1]

| SCR Process | Annual Revenue Requirements ($ $\times$ $10^{-6}$) | | | |
|---|---|---|---|---|
| | SCR | FGD | ESP | Overall |
| SFGT | 33.6 | – | 3.0 | 36.6 |
| Hitachi Zosen | 10.2 | 14.7 | 2.2 | 27.1 |

[1]All costs except the HZ-SCR and the SFGT-SCR costs are from "Preliminary Economic Analysis of $NO_x$ Flue Gas Treatment Processes". Tennessee Valley Authority - Office of Power. EPA - 600/7-80-021, February 1980.

## 5.6 OVERALL EVALUATION OF THE HZ PROCESS

The preceding discussion has examined many factors which influence the technical and economic feasibility of applying the HZ process to a coal-fired boiler. These factors include:

- the pilot plant test results,
- the results of Radian's Independent Tests,

- the results of the 500 MW conceptual design,

- the material balance calculations for the 500 MW
  HZ process application,

- the energy balance calculations for the 500 MW HZ
  process application, and

- the estimated capital investment and annual revenue
  requirements for the 500 MW HZ process application.

In order to put all these factors into perspective and thereby complete the evaluation of the HZ process, a summary of the most significant results was prepared. This summary, which is presented in the following discussion, identifies how the results of the tests and calculations influence the feasibility of applying the HZ process to a coal-fired power plant. In addition, the summary identifies areas not addressed during the pilot plant tests.

5.6.1 Pilot Plant Test Results

The major objective of the pilot plant tests conducted by Chemico was to demonstrate 90 percent $NO_x$ reduction during 90 days of continuous operation. This objective was met and exceeded during the tests with the NOXNON 600 catalyst. The pilot plant operated for 90 days and averaged over 90 percent $NO_x$ reduction and over a 6 month period, $NO_x$ reduction averaged 89.8 percent.

Some other significant results of the test program showed that neither temperature nor flowrate has as significant effect on $NO_x$ reduction efficiency within a range about the design level. These results indicate that process performance should not be impaired at boiler loads below the design level. As a result, no temperature or flow control would be required for a full-scale application of the HZ process.

During the test program, 3 charges of catalyst were examined and two of these (NOXNON 500) experienced severe plugging problems after about 2000 hours of operation. When replaced with the NOXNON 600 catalyst, which has larger gas

passages, no further plugging problems were observed. The original plugging was believed to be due to the adhesiveness of the fly ash. At high temperatures fly ash sample collected from the power plant were found to agglomerate.

Tests with the NOXNON 500 catalyst did not last long enough to get a good measure of catalyst activity, but results of the NOXNON 600 tests showed a gradual decline in catalyst activity with time. After 5500 hours of operation, activity of the NOXNON had dropped slightly, but it was still possible to achieve 90 percent $NO_x$ reduction. Since 5500 hours is close to one year of operation ($\sim$7000 hours) a catalyst life of 1 year seems reasonable based on the test results. In fact, catalyst life may be extended well beyond 1 year based on the results of the in situ regeneration test conducted at the conclusion of the test program. These tests showed the catalyst activity had been restored to the activity of essentially new catalyst. Unfortunately, since the regeneration test was conducted during the final week of the test program, it is uncertain how long the effects of regeneration would last.

Overall, the results of the pilot plant tests indicate application of the HZ process to a coal-fired boiler is technically feasible. The tests demonstrated the ability of the process to achieve 90 percent $NO_x$ reduction for over 90 days and also demonstrated a useful catalyst life of nearly one year.

5.6.2 Results of the Independent Evaluation Test Program .

The independent evaluation test program conducted by Radian had two primary objectives: to insure the quality of the data collected at the HZ pilot plant, and to quantify changes in the concentration of certain pollutants across the HZ reactor. As discussed earlier, the results of the quality assurance audits and certification tests validated the process data collected by Chemico. These results have no direct bearing on the overall feasibility of the HZ process with one exception. As a result of the inability to monitor $NH_3$ in the flue gas, the $NH_3$ emission measurements, made as part of the QA

audits, represent a significant portion of the data base on $NH_3$ emissions from the process. These data, in conjunction with the results of the secondary emissions sampling tests, quantify the secondary environmental impact associated with the HZ process as it was operated during the pilot unit tests.

The results of the secondary emissions sampling program indicated that no measurable change occurred in the concentrations of trace elements in the particulates passing through the reactor or in the concentrations of hydrocarbons, CO, HCN, or nitrosoamines in the flue gas. In the case of particulates, the results show that no environmental problem will occur due to erosion (if any) of the catalyst. In the case of HCN and nitrosoamines, the concentrations of these compounds were below the detection limit of the analytical techniques employed and were also below the maximum safe concentrations for emission sources. Again, this indicates that no environmental problem will occur due to production of these compounds.

Another result of the secondary emissions sampling program was that $SO_3$ is produced in the reactor as a result of $SO_2$ oxidation. This can cause significant operational impacts in downstream equipment such as the air preheater. The significance of the increase in flue gas $SO_3$ concentration across the reactor is magnified because of the high $NH_3$ concentrations measured at the outlet of the reactor. $NH_3$ and $SO_3$ will react to form ammonium sulfates in the air preheater which can result in plugging and corrosion. The severity of the problem depends on the actual compound formed – ammonium bisulfate is much more corrosive and more prone to cause plugging since it exists as a liquid at air preheater temperatures while ammonium sulfate exists only as a solid.

The most significant factor in determining which ammonium compound will form is the $NH_3$ to $SO_3$ mole ratio. At $NH_3/SO_3$ mole ratios below 2.0, some liquid ammonium bisulfate will form since there is not enough $NH_3$ to completely react with the $SO_3$ present. Because of this, the production of $SO_3$ in the Hitachi Zosen reactor will promote ammonium bisulfate formation and the associated problems of plugging and corrosion. And the high levels of $NH_3$ and

$SO_2$ expected at the reactor outlet will result in the formation of significant quantities of ammonium sulfates which are expected to cause severe problems in the air preheater.

Any ammonium sulfates which do not deposit in the preheater should solidify and be collected in an ESP. Previous studies have indicated that environmental problems can result from high $NH_3$ concentrations in fly ash depending on the specifics of fly ash disposal techniques. However, for most applications, no environmental problems would be expected.

One compound scheduled to be measured during the secondary emissions sampling program was $N_2O$. However, the analytical technique used to make the $N_2O$ measurements proved unsatisfactory. Therefore, no determination was made on whether any significant quantity of $N_2O$ was being produced in the reactor. Any future development work on the HZ process should include provisions for measurement of $N_2O$.

Overall, the independent evaluation tests indicated that:

- no emissions problems resulted from application of the HZ process with the exception of $NH_3$ and $SO_3$,

- the levels of $NH_3$ and $SO_3$ emissions measured during the pilot plant tests will cause severe operational problems in the air preheater,

- the estimated $NH_3$ emissions from the HZ process may result in environmental problems depending on the specific details of the fly ash disposal techniques. However, for most applications, no problems are expected, and

- it was not possible to determine the concentration of $N_2O$ (if any) in the reactor outlet. This requires further investigation.

## 5.6.3 Results of the 500 MW Conceptual Design

The conceptual design of the HZ process was prepared for a single application of the process and it was based solely on the pilot plant test results. The results of this design indicate that it is possible to reduce $NO_x$ emissions by 90 percent using the HZ process. In fact, 90 percent $NO_x$ reduction was possible at space velocities greater than previous estimates indicated (i.e., at a relatively lower catalyst volume per unit volume of flue gas treated). However, the greater space velocities were accompanied by $NH_3$ emissions which were much higher than previous estimates.

One result of the high $NH_3$ emissions estimated for the conceptual design was that special modifications to the air preheater are required to mitigate problems associated with the formation of ammonium sulfates downstream of the reactor. These modifications were identified as part of a prior study by Radian and they are based on Japanese experience with air preheater operation downstream of an SCR system. It should be noted that the modifications specified for the air preheater were expected to minimize problems at relatively low $NH_3$ and $SO_3$ concentrations at the reactor exit. The concentrations at the reactor outlet for the conceptual design are much higher than anticipated in previous studies of SCR technology and this could result in operational problems which cannot be minimized by the preheater modifications included in the conceptual design. This represents an area which requires further investigation.

Reactor pressure drop and other design parameters are fairly consistent with previous estimates for the process. The design results also show that the process can operate over a range of temperatures (340° to 410°C) and space velocities (7,600 to 10,400 hr⁻) without any significant effect on $NO_x$ reduction efficiency. This indicates the process has good flexibility in processing flue gas under conditions of changing boiler load.

In summary, the conceptual design indicates that the HZ process can reduce $NO_x$ emissions by 90 percent. And, this $NO_x$ reduction efficiency can be achieved at a lower catalyst volume per unit of flue gas treated than previous estimates indicated. However, the lower catalyst volume of the conceptual design is accompanied by a significantly higher $NH_3$ emission rate which can result in severe operational problems in downstream equipment, particularly the air preheater. Further work is required to determine if the effects of these $NH_3$ emissions can be offset by the air preheater modifications included in the conceptual design.

## 5.6.4 Results of the Material Balance Calculations

Material balance calculations for a 500 MW application of the HZ process were included as part of this study to identify raw material requirements for the process and to serve as a basis for the cost estimate which was presented in Section 5.5. The material balance was based on the pilot plant and secondary emissions sampling test results and thus reflects those results in the estimated raw material requirements. The most significant results of the material balance calculations include estimation of $NH_3$ requirements for $NO_x$ reduction, $NH_3$ and $SO_3$ emissions from the process, and steam requirements for air preheater soot blowing.

The $NH_3$ requirements for the process were estimated to be 1.0 mole of $NH_3$ per mole of $NO_x$ in the flue gas entering the reactor. This requirement was estimated based on the results of 5 months of pilot plant operation. During that 5 month period, the $NH_3/NO_x$ injection ratio averaged 0.98 while the $NO_x$ reduction efficiency averaged 89.8 percent. With the $NH_3/NO_x$ injection ratio of 1.0, estimated $NH_3$ requirements for the process decreased about 10 percent from previous estimates.

Estimates of $NH_3$ and $SO_3$ emissions from the HZ process were significantly higher than previous estimates indicated. As discussed earlier, this results in the requirements for air preheater modifications and additional soot blowing. The requirement for additional soot blowing results in a sevenfold increase in

HZ process steam requirements. However, this is not very significant from
a material balance standpoint, but it is important in terms of its effect
on process energy requirements.

In summary, the material balance calculations showed no significant
change in raw material requirements for the HZ process. The most important
result was the estimated $NH_3$ and $SO_3$ emission rates which were significantly
higher than previous estimates indicated.

## 5.6.5 Results of the Energy Balance Calculations

An energy balance was completed as part of the evaluation of the HZ
process. This energy balance defined overall process energy requirements and
quantified the heat credits associated with the process. The results of the
analysis of energy requirements indicated that the HZ process has a net
energy consumption equivalent to 0.3 percent of the energy input to the
boiler.

Energy requirements for the HZ process are about equally divided between
steam and electrical energy, each representing about 0.3 percent of the boiler'
capacity. The heat credit for the process is also about 0.3 percent of the
boiler's capacity resulting in a 50 percent reduction in process energy require
ments.

Overall, the energy requirements of the HZ process represent only a very
small fraction of the boiler's capacity. Even without the heat credit, these
requirements do not significantly influence process costs.

## 5.6.6 Results of the Cost Estimate for the 500 MW Hitachi Zosen Process Application

An estimate of total capital investment and annual revenue requirements
for a 500 MW application of the HZ process was prepared as part of this
evaluation. The estimated costs reflect the results of the pilot plant tests.

When compared with the previous estimate prepared by TVA, the modified cost estimates indicate the magnitude of the impact the pilot plant results had on estimated process costs. In addition, comparison of the modified cost estimate with a cost estimate for the SFGT process is a relative indicator of the cost effectiveness of the HZ process as tested in the pilot plant.

The capital costs for the HZ process were estimated to be $22.1 \times 10^6$ which represents a slight decrease compared to TVA's preliminary estimate. This decrease is due to the reduced catalyst volume required for the conceptual design as compared to TVA's design. It should be noted that the change in capital costs is not significant when the accuracy of the estimates is considered. Also, the costs which are associated with the high $NH_3$ and $SO_3$ emissions from the HZ process may be considerably higher than the costs included in the estimate based on the pilot plant test results.

The estimated annual revenue requirements for the HZ process were $10.2 \times 10^6$/yr which again represent a slight decrease compared to TVA's preliminary estimate. This decrease is also due to the reduction in catalyst volume for the conceptual design based on the pilot plant test results. Another major factor in determining the annual revenue requirements for the HZ process is the useful catalyst life. The cost estimate prepared as part of this study assumed a 1-year life, but this was not demonstrated during the test program.

Table 5-15 presents estimated annual revenue requirements as a function of catalyst life. As shown, a 6-month catalyst life results in about a 50 percent increase in costs compared to the base case (1-year life) while a 2-year life results in a 25 percent decrease in costs. Obviously, if a 2-year catalyst life could be demonstrated, a significant reduction in annual revenue requirements would result. It should be noted that the 6-month catalyst life is just an example and that Hitachi Zosen will guarantee a 1-year life for coal-fired process applications.

TABLE 5-15.  ESTIMATED ANNUAL REVENUE REQUIREMENTS AS A
FUNCTION OF CATALYST LIFE

| Catalyst Life | Annual Revenue Requirements $ x $10^{-6}$ |
|---|---|
| Base Case (1 year) | 10.3 |
| 6 months | 15.6 |
| 2 years | 7.7 |

Overall the results of the modified cost estimate indicate that, for the particular application examined in this study, the HZ process is economically competitive with other SCR processes.  This is based on a conceptual design which was representative of operating conditions demonstrated during the pilot plant tests.  It should be noted, however, that the costs can be affected by the impacts of high $NH_3$ and $SO_3$ emissions whose effects were not examined during the pilot plant tests.  Additionally, the estimates presented in this evaluation were based on a 1-year catalyst life which was not demonstrated.  Because of these two factors, HZ process costs could vary significantly from those estimated in this study.  Further development work should focus on defining the useful catalyst life and on demonstrating techniques for minimizing the operational impacts of high $NH_3$ and $SO_3$ emissions.

5.6.7  Process Evaluation Summary

The preceding discussion has identified the factors which influence the technical and economic feasibility of the HZ process along with some of the limitations of this evaluation.  This section summarizes the most significant aspects of the evaluation and presents an overall conclusion concerning the technical and economic feasibility of applying the HZ process to a coal-fired power plant.

The most significant results of the pilot plant test program and this evaluation are:

- ·The HZ process can reduce $NO_x$ emissions by 90 percent when applied to a coal-fired boiler. This level of emissions reduction was achieved over a 90 day period at an $NH_3/NO_x$ injection ratio of 1.0 and space velocities greater than previous test work indicated. However, the excellent performance of this pilot plant was accompanied by $NH_3$ emissions which were much higher than previous estimates indicated.

- The initial tests of the HZ process experienced problems with catalyst plugging which resulted in failure of 2 charges of NOXNON 500 series catalyst. These problems were eliminated by employing NOXNON 600 series catalyst (a catalyst with larger gas passages) and the use of compressed air (as opposed to superheated steam) for reactor soot blowing. Using the NOXNON 600 catalyst, about 5500 hours of operation were logged without signs of catalyst plugging.

- A gradual decline in catalyst activity was recorded over the duration of the test program which resulted in the requirement for increased $NH_3/NO_x$ injection ratios to attain 90 percent $NO_x$ reduction. Because the test program was terminated after 5500 hours of operation, the catalyst activity after 1 year of operation could not be determined. Determination of the useful catalyst life is important in defining the capital costs into annual revenue requirements for the HZ process.

- A novel, in situ catalyst regeneration technique was tested as part of the program. This test showed that the regenerated catalyst had activity similar to fresh catalyst and thus reversed some of the decline in activity observed over the duration of the test program. Unfortunately, the catalyst regeneration technique was tested toward the end of the pilot plant test program and so it is uncertain how long the effects of the catalyst regeneration will last. Obviously the catalyst regeneration technique has the potential to significantly reduce process costs and this merits further investigation

- The independent evaluation test program indicated that emission rates of most pollutants were not affected by the HZ process. However, emission rates of both $NH_3$ and $SO_3$ will be relatively high and those emissions can result in severe operational problems in downstream equipment. The severity of any problems is very site specific and could not be assessed as part of this study. This should, however, be given careful consideration in any planned applications of the HZ process.

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- The conceptual design and material balance calculations indicated high $NH_3$ emission rates which will cause severe operational problems in the air preheater located downstream of the HZ process. The conceptual design included air preheater modifications designed to minimize those problems. But because the estimated $NH_3$ and $SO_3$ emission rates are much higher than previous estimates, it is uncertain if the air preheater modifications will prove adequate. Further investigation in this area is required.

- The overall energy requirements for the HZ process were estimated to be 0.3 percent of the boiler's capacity. This is a very small fraction of boiler capacity and it does not significantly affect process costs.

- The estimated capital investment and annual revenue requirements for the HZ process were slightly lower than TVA's preliminary estimate. This indicates that the HZ process is economically competitive with other SCR processes when considered for operation to a coal-fired boiler. It should be noted that the cost estimates assumed a 1-year catalyst life which was not quite demonstrated during the pilot plant tests. The relative process costs could change if a 1-year catalyst life is not possible.

In conclusion, the pilot plant test results indicate the HZ process is technically suited for application to coal-fired sources. However, the tests did not demonstrate a 1-year catalyst life which is generally considered a minimum for technical feasibility of an SCR process. In reality, a shorter catalyst life would translate into increased annual revenue requirements. In terms of costs, under the conditions of the cost estimate prepared as part of this study, the HZ process is economically competitive with other SCR processes.

# SECTION 6

## PROCESS DEVELOPMENT REQUIREMENTS


The pilot plant test results and the evaluation completed as part of this study have defined many of the factors which affect the technical and economic feasibility of applying the HZ process to a coal-fired source. However, due to limitations of the pilot plant test program, there are several key factors which were not examined. These factors represent process development requirements of varying priorities; some must be examined in further test work to establish the technical or economic feasibility of the process and some simply represent methods of improving process performance or lowering process costs. This section presents a discussion of the process development requirements identified during the course of the independent evaluation program. It also defines priorities for further investigation of those requirements.

The process development requirements identified during the course of this study include:

- Determination of catalyst life for coal fired applications of the HZ process and investigation of catalyst regeneration.

- Investigation of measures to minimize the impacts resulting from formation of ammonium sulfates downstream of the reactor.

- Quantification of $N_2O$ emissions (if any) from the process.

- Demonstration of an automatic $NH_3$ injection control system which includes a continuous $NH_3$ analyzer.

Each of these development requirements represents an area not addressed during the pilot plant tests and therefore an unanswered question concerning the HZ process. The following discussion examines each requirement in more detail

and discusses its importance in terms of the technical and economic feasibility of the HZ process.

## Catalyst Life

The useful life of the NOXNON 600 Catalyst for a coal-fired application was not determined during the pilot plant tests. The tests did show that the catalyst activity declined gradually over the deviation of the test program. But the catalyst was still able to achieve $NO_x$ reduction efficiencies of 90 percent after nearly 5500 hours of operation. In addition, the test of a method of catalyst regeneration restored catalyst activity to close to the level of new catalyst. These facts indicate that the useful life of the NOXNON 600 catalyst is close to year.

Determining the useful life of the NOXNON 600 series catalyst does not appear to be critical to either the technical or economic feasibility of the HZ process. However further investigation of catalyst life including the longer term effects of catalyst regeneration can have a significant impact on the costs of applying the HZ process. As discussed earlier, demonstration of a 2-year catalyst life would reduce annual revenue requirements of the process by 25 percent. This could make the costs of applying the HZ process significantly lower than the costs for other SCR processes.

## Impacts of Ammonium Sulfates

The high $NH_3$ and $SO_3$ emissions from the HZ process are expected to have a severe impact on an air preheater located down stream of the process. For this reason, the conceptual design of the HZ process specified air preheater modifications intended to minimize the impacts of ammonium sulfate formation. In addition, the cost estimate prepared as part of this evaluation included the captial and annualized costs associated with those air preheater modifications.

Unfortunatly, there are no data to substantiate whether the proposed air preheater modifications will be effective in mitigating the impacts of ammonium sulfate formation especially at the concentrations of $NH_3$ and $SO_3$ expected downstream of the HZ process. The air preheater modifications which were included in the conceptual design were identified as a possible solution to the ammonium sulfate problem for concentrations of $NH_3$ and $SO_3$ on the order of 30 ppm each. Therefore it is possible that, with the high concentrations of $NH_3$ and $SO_3$ expected downstream of the reactor, the proposed air preheater modifications will not be effective in controlling deposition and corrosion. If this is the case, other more costly measures may be required to help minimize the problem. This could significantly increase the estimated costs for the HZ process.

The ability of air preheater modifications to minimize the effects of ammonium sulfate deposition is an important question concerning the HZ process. Further development work is needed to determine what measures are needed to minimize the impacts of high $NH_3$ and $SO_3$ emissions and to quantify the costs associated with high emission levels.

## $N_2O$ Emissions

Originally, the secondary emissions sampling program included tests to measure $N_2O$ production in the HZ reactor. Unfortunately, the techniques used during the sampling program did not prove satisfactory and it was not possible to measure $N_2O$ in the flue gas streams. As a result, the question of $N_2O$ production in the reactor remains unanswered.

Currently there are no regulations which limit $N_2O$ emissions from stationary sources. One reason for this is because significant quantities of $N_2O$ are not produced as a result of stationary source combustion. However, production of large quantities of $N_2O$ could present problems not typically encountered. For this reason, further development work should include tests designed to characterize $N_2O$ emissions (if any) from the HZ process. Based on the poor performance of the infrared analyzer used for the secondary emissions sampling program, the recommended technique is cryogenic trapping

followed by gas chromatography analysis. This involves concentration of $N_2O$ in the gas stream followed by quantitative analysis and is routinely used to measure concentrations of $N_2O$ as low as 0.3 ppm.

Since there are no regulations which limit $N_2O$ emissions, the priority of development work designed to quantify these emissions is considered low.

## $NH_3$ Injection Control/Continuous $NH_3$ Analysis

Automatic control of the $NH_3/NO_x$ injection ratio which includes the use of continuous $NH_3$ emission measurements as feedback to such a control system represents an area not addressed during the pilot plant tests. The $NH_3$ injection control system employed during the test program was a feed foreword system. The $NH_3/NO_x$ injection ratio was set manually. The controller monitored inlet $NO_x$ and flue gas flowrate and then determined the flowrate on $NH_3$ required to achieve the desired $NH_3/NO_x$ injection ratio. This control scheme operates without regard to $NH_3$ emissions.

The type of control system which has not been demonstrated is that which uses $NH_3$ emission measurements as feedback. The reason for this is the lack of a continuous $NH_3$ analyzer. This represents a research and development requirement not only for the HZ process but for SCR processes in general.

During the pilot plant tests, Chemico attempted to measure $NH_3$ emissions continuously using a converter-analyzer system which oxidizes $NH_3$ to $NO_x$ and then measures the $NO_x$ using a chemiluminescent analyzer. This technique did not prove successful, although the exact problem(s) with the technique was never determined. Currently, there is quite a bit of research being done in Japan and the U.S. to develop a continuous $NH_3$ analyzer, but to date no technique has been demonstrated. Further work in this area should focus on evaluating the various techniques being developed and demonstrating the most

promising ones. In the case of the HZ process a feedback control of the $NH_3$ injection rate could be used to minimize potential operating problems in the air preheater.

Summary

In summary, there are development requirements for the HZ process of varying priorities. Of these, the most significant are: the determination of the useful life of the NOXNON 600 catalyst and the demonstration of techniques to minimize the impacts of high $NH_3$ and $SO_3$ emissions from the process. Both these items can have a significant impact on the estimated capital costs and annual revenue requirements of the HZ process.

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Appendix A


TECHNICAL NOTE


RESULTS OF THE QUALITY ASSURANCE
AUDITS AT THE EPA SPONSORED
$NO_x$ PILOT PLANTS




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# SECTION 1

## INTRODUCTION

The Environmental Protection Agency sponsored pilot scale tests of
two selective catalytic reduction (SCR) processes for $NO_x$ removal. The processes tested were the Hitachi-Zosen (HZ) process and the Shell flue gas
treatment (SFGT) process which also removes $SO_2$. The contractors responsible
for design and operation of these pilot units were Chemico Air Pollution
Control Corporation (HZ process) and the Process Division of UOP (SFGT
process). In both cases, these contractors were responsible for collection,
evaluation, and reporting of test data.

As part of the pilot scale test program, EPA contracted Radian Corporation
to conduct an independent evaluation of the performance of both pilot units.
This independent evaluation consisted of several steps including:

- A quality assurance program to check measurements being
  made by the process operators,

- A sampling program to quantify changes in secondary process
  emissions across the SCR reactors, and

- A program to certify the performance of the continuous $NO_x$
  monitors (and $SO_2$ monitors at the SFGT pilot unit) using
  EPA reference methods.

This technical note presents the results of the quality assurance (QA) audits
conducted to insure the quality of the major process measurements made by
Chemico and UOP. Results of the secondary emissions sampling program and the
continuous monitor certification tests are contained in separate technical
notes.

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# SECTION 2

## OBJECTIVES AND APPROACH


The objective of the Quality Assurance audits conducted by Radian was to provide an independent check of the major process measurements made on a routine basis by both UOP and Chemico. Not all process measurements were subject to audit as part of the QA program. Only those measurements which are most significant in terms of quantifying process raw material and energy requirements were audited.

Table 1 summarizes the QA audit plan. It identifies the process measurements to be audited, the planned audit frequencies, and the techniques used to conduct the QA audits at both pilot plants. As shown, these process measurements represent the most basic operating parameters required to characterize the operation of the HZ and SFGT processes. The principal raw material requirements are characterized by the quantity of $NH_3$ required to reduce a specific quantity of $NO_x$ and, in the case of the SFGT process, the quantity of $H_2$ needed to regenerate the acceptor. The major utility requirements are characterized by the power needed to overcome the reactor pressure drop and the steam required. The flue gas flowrate is required to complete material balances and to determine the capacity of the reactor and thus the costs to treat a specific volume of gas. Ammonia emissions are important since they can have potentially significant operational and economic impacts on equipment located downstream of an SCR system. And finally, flue gas $SO_2$ concentration was audited at the HZ pilot plant to document the ability of the catalyst to operate treating flue gas with relatively high $SO_2$ concentrations.

The techniques used to conduct the QA audits represent independent checks on the process measurements. In several cases the techniques used were EPA reference methods while others represent standard instruments or sampling and analytical methods. In the case of $NH_3$ emissions measurements, care was taken to insure that the formation of ammonium sulfates did not interfere with the sampling and analysis procedure.

The audit frequencies presented in Table 3-8 were selected based on several criteria. One consideration in specifying the audit frequencies was the availability/reliability of continuous process measurements. The most significant item which was not measured continuously at either pilot plant was the $NH_3$ concentration at the reactor outlet. As a consequence, the planned audit frequency for this measurement was relatively high.

Another consideration in determining the audit frequencies was the difficulty of making a particular measurement. If an audit is very time consuming then obviously this reduces the number of audits which can be conducted in a given period of time. An example of this is the $H_2$ flowrate at the SFGT pilot unit. It was expected that auditing the $H_2$ flowrate measurement would be difficult and so the frequency was lower.

It should be noted that the audit frequencies specified in Table 1 were initial frequencies and they changed as the QA program progressed. For the most part a change in audit frequency depended on the agreement between the audit result and the value of the process measurement recorded by Chemico or UOP.

Figure 1 presents a decision chain which was used as one basis for changing the initial audit frequencies, depending on the agreement between process measurements and the audit results. As shown, if the agreement was within ±5 percent, the audit frequency was decreased and the new frequency determined by the on site QA program leader. If the audit agreement was within ±10 percent of the measured value, no change in frequency was made.

TABLE 1. SUMMARY OF THE QA AUDIT PROGRAM

| Process Measurement/ Location | Pilot Plant Audited[1] | | Initial Audit Frequency (Audits/Week) | Audit Procedure |
|---|---|---|---|---|
| | HZ | SFGT | | |
| $SO_2$ Concentration/ Reactor Inlet | X | | 2 | EPA Method 6 |
| Flue Gas Flowrate | X | X | 3 | EPA Method 2 |
| $NH_3$ Injection Rate | X | X | 3 | Absorption followed by weight gain measurement – analogous to EPA Method 4 |
| Reactor Pressure Drop | X | X | 3 | Magnehelic differential pressure gauge |
| Reactor Operating Temperature | X | X | 3 | Thermocouple with traverse of gas duct |
| $NH_3$ Concentration/ Reactor Outlet | X | X | 10 | Absorption, distillation and titration |
| Steam Flowrate | | X | 0.5 | Calibration of orifice plate |
| $H_2$ Flowrate | | X | 0.5 | |

[1]X indicates an audit was scheduled.
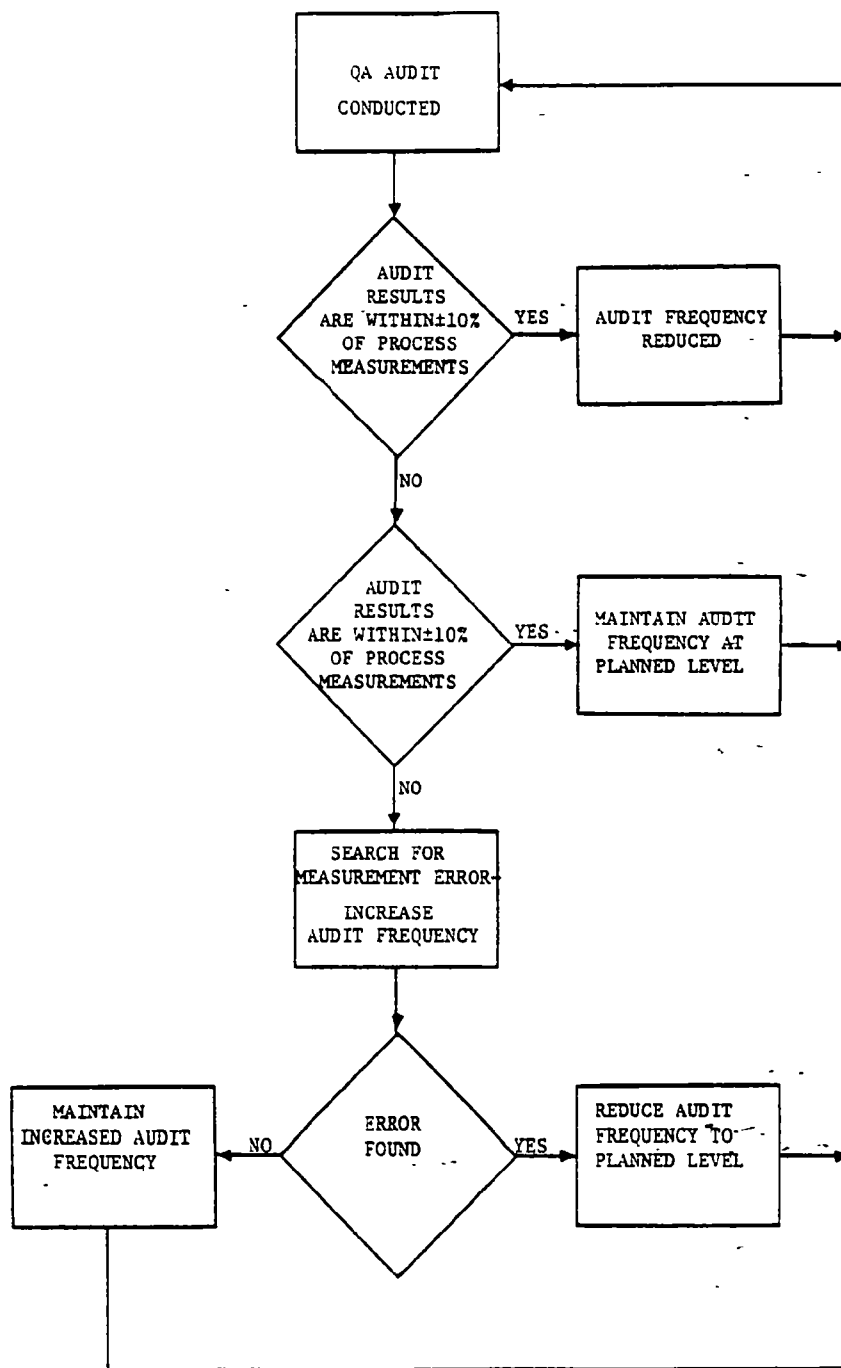
Figure 1.  Action plan based on QA audit results.

If the audit agreement was outside the ±10 percent range, corrective action was initiated to determine the source of error in either the audit procedure or the process measurement. At the same time, the audit frequency was increased. If the source of error was found and corrected, the audit frequency was reduced. However, if the error could not be resolved, the audit frequency was maintained at the maximum practical level within the time and manpower limits of the program. In addition to the use of relative accuracy of the QA audits as a basis for modifying the audit frequency, several practical considerations resulted in the reduction of the audit frequencies. These are discussed in Section 3.

SECTION 3

RESULTS OF THE QA AUDITS


The planned QA audits and the audit procedures were outlined in Section 2
of this technical note. This section presents a summary of the QA audits
and details of individual audit results. It also includes a brief discussion
of the results.


## Summary


Table 2 summarizes the QA audit results from both the HZ and the SFGT
pilot plants. As shown, most of the QA audit results were within 10 percent
of the process measurements made by UOP and Chemico. This indicates that these
process measurements were accurate and the test data collected can be used to
characterize process operation.


Two measurements which did not show good agreement with the QA audits
were the $SO_2$ concentration at the HZ pilot plant and the flue gas flowrate
at the SFGT pilot plant. In both cases, subsequent investigation resolved the
discrepancy between the process measurements and the QA audits.


In the case of the flue gas $SO_2$ concentration at the HZ pilot plant,
the audit results were determined to be correct and the $SO_2$ monitor was in
error. This error is characteristic of the type of $SO_2$ monitor used (pulsed
fluorescence) when the instrument is calibrated with standard gases composed
of $SO_2$ in nitrogen. The response of a pulsed fluorescence $SO_2$ monitor to
$SO_2$ in a gas stream is quenched by the presence of $O_2$ and $CO_2$. This means
that addition of $O_2$ and $CO_2$ to a gas stream contining $SO_2$ and $N_2$ will result
in an apparent reduction in the concentration of $SO_2$ as measured by a pulsed

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TABLE 2. RESULTS OF THE QA AUDITS AT BOTH THE
HZ AND SFGT PILOT PLANTS

| Process Measurement/ Location | Planned Audit Frequency (Audits/Week) | Relative Error(%) | Actual Frequency (Audits/Week) | Relative Error(%) | Actual Frequency (Audits/Week) |
|---|---|---|---|---|---|
| $SO_2$ Concentration/ Reactor Inlet | 2 | -19.8 | 2 | NA[1] | NA |
| Flue Gas Flowrate | 3 | -0.3 | 2 | -14.4 | 2.5 |
| $NH_3$ Injection Rate | 3 | -6.0 | 1 | 7.6 | 1 |
| Reactor Pressure Drop | 3 | 4.5 | 2 | -1.4 | 2 |
| Reactor Operating Temperature | 3 | 4.8 | 2 | -1.3 | 2 |
| Steam Flowrate | 0.5 | NA | NA | ND[2] | 0 |
| $H_2$ Flowrate | 0.5 | NA | NA | ND | 0 |

[1]NA - Not Applicable

[2]ND - Not Determined

fluorescence analyzer. The error which results from calibration with $SO_2$-$N_2$
mixtures (this was done at the HZ pilot plant) can be as high as 30 percent.

In the case of the flue gas flowrate measured at the SFGT pilot plant,
the audit was determined to be in error. Because of the discrepancy between
the process measurement and the audit result, UOP made an independent check
of the flue gas flowrate measurement. The results of this independent check
agreed very well with the process measurement results. It was concluded that
the duct area used to calculate flowrate for the EPA Method 2 tests (velocity
traverse) was in error. This may have been due to a measurement error or
blocking of a portion of the duct crossection by fly ash.

Table 2 does not present the results of $NH_3$ emission tests conducted
at the pilot plants. These results are contained in Appendix B with the
secondary emissions sampling results. The reason for this is that continuous
$NH_3$ monitor at both pilot plants did not work and so, the $NH_3$ emission "audit
results" represented a large fraction of the $NH_3$ emission measurements at both
pilot plants and were not actually audits. (Both Chemico and UOP did conduct
batch sampling and analysis tests for $NH_3$).

Table 2 also indicates that two measurements scheduled to be audited
were not. Both the steam and $H_2$ flowrates were not audited because it was
not possible to do so without shutting down the SFGT pilot plant operation.
However, following the completion of the demonstration tests, the orifice
plates used to measure steam and $H_2$ flowrates were calibrated by UOP personnel.

Finally the planned and actual audit frequencies are presented in Table 2.
As shown, most of the actual audit frequencies are lower than the planned
frequencies. There are several reasons for this discrepancy. In the case of
reactor pressure drop, the flue gas inlet temperature, and the flue gas flow-
rate at the HZ plant, the agreement was excellent (±5 percent), and the
frequency was reduced according to the decision chain shown in Figure 1. In
the case of $NH_3$ injection rate, the agreement was good (±10 percent) and the

difference was constant so no benefit was derived from a large number of audits. At the SFGT pilot plant, the audit frequency for the flue gas flow-rate was ultimately limited by access to the flue gas stream. The sampling locations at the reactor inlet and outlet had to be shared between personnel conducting the QA audits and those conducting the stack sampling and continuous monitor certification tests.

Only the audit frequency for flue gas $SO_2$ concentration was as originally scheduled. However, the QA plan called for an increase in audit frequency if the relative error was greater than 10 percent. The audit frequency was not increased in this case since the difference between the $SO_2$ monitor results and the QA audits was relatively constant.

Overall, the QA audit results indicated that the process measurements made at both pilot plants were accurate. One exception was the $SO_2$ measure-ments at the HZ pilot plant. The audit results and subsequent investigation revealed the $SO_2$ monitor was in error by about 20 percent. This, however, does not affect the overall process evaluation since $SO_2$ was measured to document the concentration of $SO_2$ the catalyst was exposed to and not as a key process parameter.

The following discussion presents the results of individual QA audits.

SO$_2$ Concentration

Table 3 presents the results of the QA audits of the flue gas $SO_2$ monitor at the HZ pilot plant. As shown, the relative error was quite high averaging nearly 20 percent.

TABLE 3.   HZ SO$_2$ MONITOR QA AUDIT RESULTS

| Test No. | Continuous Monitor (ppm) | Method 6 (ppm) | Error (%) |
|---|---|---|---|
| 1 | 990 | 1248 | -20.7 |
| 2 | 1000 | 1271 | -21.3 |
| 3 | 960 | 1256 | -23.6 |
| 4 | 990 | 1207 | -18.0 |
| 5 | 1000 | 1156 | -13.5 |
| 6 | 960 | 1216 | -21.1 |
| Average | 983 | 1226 | -19.8 |

This was due to the quenching effect of $O_2$ and $CO_2$ on the pulsed fluorescence monitor used to measure flue gas SO$_2$ concentrations at the HZ pilot plant. Investigators conducted an analysis of pulsed fluorescence analyzers and determined the error could be as high as 30 percent. The following equation was developed to correct the monitor's results based on the flue gas composition.

$$(K_{SO_2} \cdot P_{SO_2} + K_f)(I_o/I-1) = P_{O_2} \cdot K_{O_2} + P_{CO_2} \cdot K_{CO_2} + (P_{N_2} - 760 \ I_o/I)K_{N_2}$$

Where  $I_o$  =  Intensity without quenching

$I$  =  Intensity with quenching

$K_i$  =  Quenching rate for species i (i.e., SO$_2$, O$_2$, CO$_2$, N$_2$)

$P_i$  =  Partial pressure of species i

$K_f$  =  Fluorescence decay rate

Using the average flue gas composition and solving this equation for $I_o$, the corrected SO$_2$ concentration can be estimated. However, experimental values for $K_i$'s need to be determined. These data are not available at this time.

As a rough estimate, the results of the QA audits of the SO$_2$ monitor indicate that the SO$_2$ concentrations measured by Chemico were 20 percent

lower than the actual flue gas concentration.  Fortunately, these data do not affect the overall process evaluation.

### Flue Gas Flowrate

The results of the flue gas flowrate QA audits at the HZ and SFGT pilot plants are presented in Tables 4 and 5 respectively.  As shown, the flowrate audits at the HZ pilot plant were in excellent agreement with the measurements made by Chemico, indicating that the process measurements were accurate. However, the flowrate measurements at the SFGT pilot plant did not agree with the audit results.  As discussed earlier, it appears that the audit result was inaccurate.  The consistent error between the process measurements and the audit results indicates that the actual audit measurement (flue gas velocity rather than flowrate) was accurate and a consistent error was introduced in the flowrate calculation.  The most likely explanation for this is that an inaccurate value for the duct crossection was used in the flowrate calculations.

The QA flowrate audit results indicate that accurate flowrate measurements were made at both the HZ and SFGT pilot plants.

TABLE 4.  HZ FLUE GAS FLOWRATE QA AUDIT RESULTS

| Test No. | Flowmeter (scfm) | Audit - Method 2 (scfm) | Error (%) |
|----------|------------------|--------------------------|-----------|
| 1 | 1324 | 1310 | 1.1 |
| 2 | 1341 | 1318 | 1.7 |
| 3 | 1345 | 1327 | 1.4 |
| 4 | 1542 | 1576 | -2.2 |
| 5 | 1524 | 1568 | -2.8 |
| Average | 1415 | 1420 | -0.3 |

TABLE 5.   SFGT FLUE GAS FLOWRATE QA AUDIT RESULTS

| Test No. | Flowmeter (scfm) | Audit - Method 2 (scfm) | Error (%) |
|----------|------------------|-------------------------|-----------|
| 1 | 987 | 1102 | -10.4 |
| 2 | 986 | 1204 | -18.1 |
| 3 | 978 | 1165 | -15.3 |
| 4 | 1026 | 1186 | -13.5 |
| 5 | 1023 | 1236 | -17.2 |
| 6 | 984 | 1290 | -23.7 |
| 7 | 992 | 1123 | -11.7 |
| 8 | 984 | 1085 | -9.3 |
| 9 | 1000 | 1116 | -10.4 |
| 10 | 1000 | 1126 | -11.2 |
| Average | 996 | 1163 | -14.4 |

## NH₃ Injection Rate

The results of the NH$_3$ injection rate QA audits at both the HZ and SFGT pilot plants are presented in Table 6.  As shown, the relative error at both plants was consistent and had the same magnitude.  This error was within the accuracy limits of the measurement technique (i.e., absorption followed by weight gain measurement).  The results indicate that accurate (±10 percent) NH$_3$ injection measurements were made at both pilot plants.

TABLE 6.  NH$_3$ INJECTION RATE AUDITS AT THE HZ AND SFGT PILOT PLANTS

| Test No. | Process Measurement (gms NH$_3$/min) | Audit-Absorption (gms NH$_3$/min) | Error % |
|---|---|---|---|
| HZ Pilot Plant | | | |
| 1 | 11.8 | 12.7 | -7.1 |
| 2 | 11.9 | 12.5 | -4.8 |
| Average | 11.85 | 12.6 | -6.0 |
| | | | |
| SFGT Pilot Plant | | | |
| 1 | 10.4 | 9.7 | 6.9 |
| 2 | 9.7 | 9.0 | 7.3 |
| 3 | 9.8 | 9.1 | 7.8 |
| Average | 9.97 | 9.27 | 7.6 |

## Reactor Pressure Drop

The results of the reactor pressure drop QA audits at the HZ and SFGT pilot plants are presented in Tables 7 and 8, respectively. As shown, the process measurements and audit results at both pilot plants were in excellent agreement. This indicates that the pressure drop measurements made by Chemico and UOP during the pilot plant test program were accurate.

TABLE 7.  HZ REACTOR PRESSURE DROP AUDIT RESULTS

| Test No. | Process Measurement. (in H$_2$O) | Audit-Magnehelic (in H$_2$O) | Error (%) |
|---|---|---|---|
| 1 | 1.05 | 1.0 | 5.0 |
| 2 | 1.05 | 1.0 | 5.0 |
| 3 | 1.04 | 1.0 | 4.0 |
| 4 | 1.04 | 1.0 | 4.0 |
| 5 | 1.04 | 1.0 | 4.0 |
| 6 | 1.05 | 1.0 | 5.0 |
| Average | 1.045 | 1.0 | 4.5 |

TABLE 8. SFGT REACTOR PRESSURE DROP AUDIT RESULTS

| Test No. | Process Measurement (in $H_2O$) | Audit-Magnehelic (in $H_2O$) | Error (%) |
|----------|------------------------|-----------------------|-----------|
| 1 | 10.75 | 10.5 | 2.4 |
| 2 | 10.75 | 10.5 | 2.4 |
| 3 | 10.25 | 11.0 | -6.8 |
| 4 | 10.00 | 10.5 | -4.8 |
| 5 | 9.75 | 10.0 | -2.5 |
| 6 | 9.50 | 9.75 | -2.6 |
| 7 | 10.50 | 10.25 | 2.4 |
| Average | 10.21 | 10.36 | -1.4 |

## Reactor Operating Temperature

The results of the reactor operating temperature QA audits at the HZ and SFGT pilot plants are presented in Tables 9 and 10 respectively. As shown, the process measurements and the audit results at both plants were in excellent agreement. This indicates that the reactor inlet temperatures measured by Chemico and UOP were accurate. Since Chemico demonstrated reactor performance over a range of temperatures, these results are not critical to the HZ process but they are to the SFGT process. UOP did not document SFGT process performance at reduced temperatures, so the process measurements define a lower limit for process operation.

TABLE 9. HZ REACTOR OPERATING TEMPERATURE AUDIT RESULTS

| Test No. | Process Measurement (°F) | Audit Thermocouple (°F) | Error (%) |
|----------|--------------------------|-------------------------|-----------|
| 1 | 717 | 681 | 5.3 |
| 2 | 720 | 691 | 4.2 |
| 3 | 719 | 684 | 5.1 |
| 4 | 722 | 690 | 4.6 |
| 5 | 718 | 684 | 5.0 |
| Average | 719.2 | 686 | 4.8 |

TABLE 10. SFGT REACTOR OPERATING TEMPERATURE AUDIT RESULTS

| Test No. | Process Measurement (°F) | Audit Thermocouple (°F) | Error (%) |
|---|---|---|---|
| 1 | 772 | 780 | -1.0 |
| 2 | 762 | 769 | -0.9 |
| 3 | 781 | 794 | -1.6 |
| 4 | 781 | 790 | -1.1 |
| 5 | 785 | 769 | 2.1 |
| 6 | 787 | 801 | -1.7 |
| 7 | 780 | 802 | -2.7 |
| 8 | 776 | 799 | -2.9 |
| 9 | 778 | 788 | -1.3 |
| Average | 778 | 788 | -1.3 |

Appendix B

TECHNICAL NOTE

·RESULTS OF SECONDARY
EMISSION SAMPLING
AT THE
EPA SPONSORED NO$_x$ PILOT PLANTS

December, 1980

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SECTION 1

INTRODUCTION


The Environmental Protection Agency sponsored pilot scale tests of two selective catalytic reduction (SCR) processes for $NO_x$ removal. The processes tested were the Hitachi-Zosen (HZ) process and the Shell flue-gas treatment (SFGT) process which also removes $SO_2$. The contractors responsible for design and operation of these pilot units were Chemico Air Pollution Control Corporation (HZ process) and the Process Division of UOP (SFGT process). In both cases, these contractors were responsible for collection, evaluation, and reporting of test data.


As part of the pilot scale test program, EPA contracted Radian Corporation to conduct an independent evaluation of the performance of both pilot units. This independent evaluation consisted of several steps including:

- A quality assurance program to check measurements being made by the process operators,

- A sampling program to quantify changes in secondary process emissions across the SCR reactors, and

- A program to certify the performance of the continuous $NO_x$ monitors (and $SO_2$ monitors at the SFGT pilot unit) using EPA reference methods.

This technical note presents the results of the sampling program to quantify changes in secondary process emissions. Results of the quality assurance program and the certification tests are contained in separate technical notes.

# SECTION 2

## POLLUTANTS OF INTEREST

SCR processes have been operated commercially in Japan for several years, but there is a surprising lack of data on secondary emissions from these processes. Therefore, one objective of EPA's pilot plant test-program was to quantify changes in secondary emissions across the SCR reactor. Based on available information about SCR processes and on concerns expressed by the professional community, a group of pollutants was selected for detailed sampling and analysis at the EPA sponsored pilot plants. These pollutants include:

- ammonia ($NH_3$),
- sulfur trioxide ($SO_3$),
- particulate loading and composition,
- carbon monoxide (CO),
- hydrocarbons ($C_1$ through $C_6$),
- hydrogn cyanide (HCN),
- nitrosoamines, and
- nitrous oxide ($N_2O$).

The following discussion briefly examines the reasons for measuring each of these pollutants, while Section 3 contains a description of the pilot units and the process streams which were sampled during the test program. Section 4 presents the results of the sampling effort, along with a brief description of the sampling and analysis procedures used.

## Ammonia (NH₃)

Ammonia was measured at the reactor outlet at each pilot plant to quantify the emission rate under normal operating conditions. Ammonia is injected upstream of the catalyst in an SCR process to react with $NO_x$ reducing it to molecular nitrogen. Under normal operating conditions, it is expected that some NH₃ will pass through the catalyst unreacted. This unreacted NH₃ represents a secondary process emission which can present significant operational and possibly environmental problems, depending on the emission rate.

## Sulfur Trioxide (SO₃)

Sulfur trioxide was measured at each pilot unit to determine if any change in concentration occurs in the $NO_x$ reduction reactor. The reason for measuring SO₃ across the reactor differs for each plant. The Hitachi-Zosen system contains a catlyst which can promote oxidation and it is possible that SO₃ may be produced in the reactor due to SO₂ oxidation. On the other hand, UOP has indicated that the SFGT system may actually reduce flue gas SO₃ concentrations due to reaction with the material used in the reactor. Measurement of the SO₃ concentration at the reactor inlet and outlet was made to quantify the magnitude of any changes which occur in the reactor at both pilot plants.

## Particulate Loading and Composition

Particulate samples were collected and analyzed at the pilot units. Particulate loading was measured to document the loading the reactor is exposed to and thus demonstrate the ability of the reactor to operate under high particulate loadings. Particulate composition was measured to attempt to determine if any catalyst is being eroded from the reactor. This was done by examining particulate composition at the reactor inlet and outlet and determining if any increase in the concentration of the elements present in the catalyst occurs.

## Carbon Monoxide (CO) and Hydrocarbons (HC)

Carbon monoxide and hydrocarbons were measured at the reactor inlet
and outlet to determine if any change occurs in the concentration of these
pollutants across the reactor. These two pollutants are of interest since
they can both be oxidized by oxygen or $NO_x$. As a consequence, it is possible
that the reactor may also reduce the emission levels of CO and/or HC.

## Hydrogen Cyanide (HCN), Nitrosoamines, and Nitrous Oxide ($N_2O$)

Hydrogen cyanide, nitrosoamines and nitrous oxide were measured to
determine if any change in the concentration of these compounds occurs in
the pilot system reactors. While no concrete evidence exists to indicate
that HCN, nitrosoamines, or $N_2O$ are produced, concern has been expressed
that the presence of $NH_3$ and the catalyst may result in production of one
or more of these compounds. The sampling program was designed to measure
each of these compounds and document any change in their concentrations
across the reactor.

# SECTION 3

## PILOT PLANT DESCRIPTION

EPA has sponsored the demonstration of two SCR processes applied to coal-filled boilers. The size of these units was nominally 0.5 MWe equivalent and each was designed to remove 90 percent of the incoming $NO_x$. The SFGT pilot unit was also designed to achieve simultaneous removal of 90 percent of the $SO_2$ in the flue gas. The following discussion presents a brief description of each process in general and a specific description of the EPA sponsored pilot plants.

## 3.1 CHEMICO/HITACHI-ZOSEN PLANT

Chemico Air Pollution Control Corporation's pilot demonstration of the Hitachi-Zosen selective catlytic reduction (SCR) process is located at Georgia Power Company's Plant Mitchell Station in Albany, Georgia. The process has been commercially applied to numerous oil and gas-fired boilers in Japan. This pilot plant is a demonstration of the process for coal-fired applications.

The SCR process utilizes ammonig ($NH_3$) to selectively reduce $NO_x$ to molecular nitrogen ($N_2$) in a catalytic reactor. The overall chemical reactions are shown in Equations 1 and 2.

$$4 \ NO(g) + NH_3(g) + O_2(g) \rightarrow 4 \ N_2(g) + 6 \ H_2O(g) \qquad (1)$$

$$2 \ NO_2(g) + 4 \ NH_3(g) + O_2(g) \rightarrow 3 \ N_2(g) + 6 \ H_2O(g) \qquad (2)$$
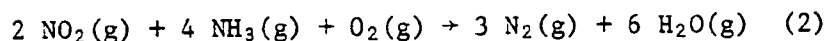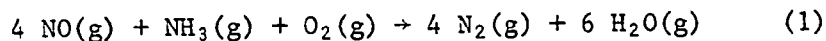
In the process, $NH_3$ is injected into flue gas which is at a temperature between 300 °C and 400 °C. The gas then passes through a catalytic reactor where the reduction reactions (Equations 1 and 2) occur rapidly.

The HZ pilot plant processed a 1000-1500 SCFM slipstream of flue gas which was withdrawn between the economizer and the air preheater of the coal-fired unit 3 at the Plant Mitchell Station. At this point, the flue gas contained the full particulate loading from the boiler. The slipstream from the boiler was first passed up through a flue gas heater for temperature control. $NH_3$ was then injected into the flue gas which flowed down through the reactor. After exiting the reactor, the gas passed through a cyclone particulate collector, a fan, and it then returned to the boiler flue gas duct. The particulate collector was included in the pilot unit to minimize abrasion in the fan.

Figure 1 is a schematic of the HZ pilot plant which shows the location of the sampling ports used during the test program. The flue gas temperature was approximately 315 °C at the inlet sample port and 370 °C at the outlet port. Full particulate loadings were present at both sampling locations.
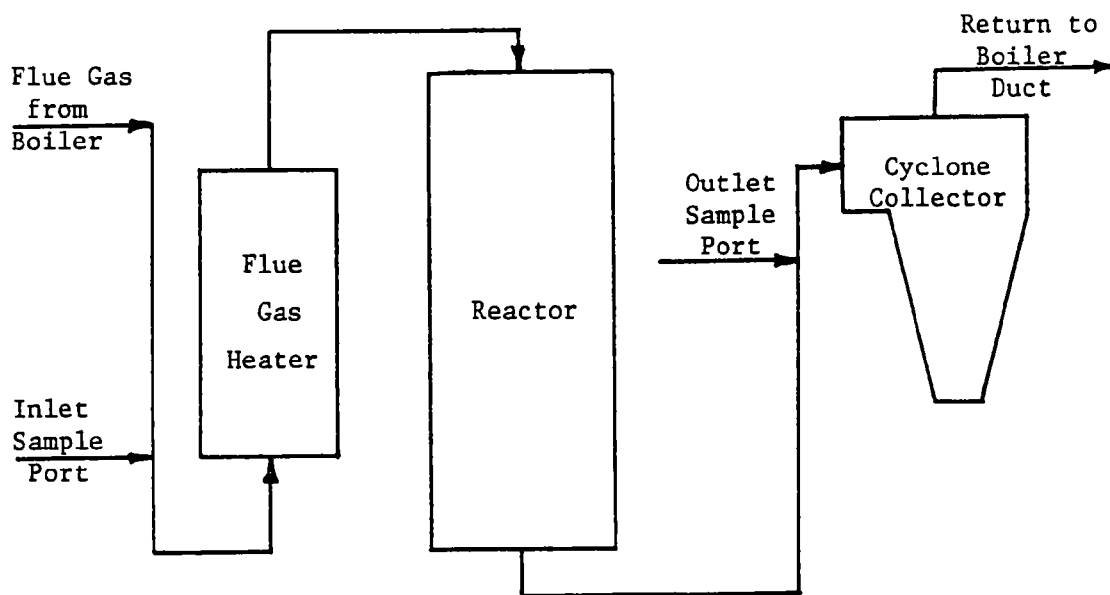


Figure 1.  Schematic of the HZ pilot plant.

## 3.2 UOP/SFGT PILOT PLANT

The Process Division of UOP has operated a pilot demonstration of the Shell Flue Gas Treatment (SFGT) process at Tampa Electric Company's Big Bend Station in North Ruskin, Florida. The process has been commercially applied on an oil-fired boiler in Japan, while the pilot plant was a coal-fired demonstration.

This SCR process is unique in that it removes both $SO_2$ and $NO_x$. Copper supported on alumina is used as an $SO_2$ "acceptor". $SO_2$ and $O_2$ react with the acceptor as shown in Equation 3.

$$SO_2(g) + \tfrac{1}{2} O_2(g) + CuO(s) \rightarrow CuSO_4(s) \qquad (3)$$
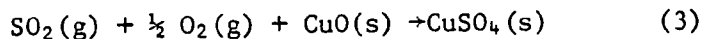
Copper oxide and, to a greater extent, the copper sulfate ($CuSO_4$) produced by the $SO_2$ acceptance reaction, act as a catalyst for the reduction of $NO_x$ by $NH_3$ according to Equations 1 and 2.

As $SO_2$ is removed in the reactor, the acceptor becomes "loaded" and $SO_2$ emissions begin to increase. Once the time averaged $SO_2$ removal reaches the design level (e.g., 90 percent), flue gas flow to the reactor is shut off and the $CuSO_4/CuO$ are reconverted to Cu metal. In this regeneration step, a steam/hydrogen mixture is passed through the reactor and a concentrated $SO_2$ stream is produced. The regeneration reactions are illustrated by Equations 4 and 5.

$$CuSO_4 + H_2 \rightarrow CuO + SO_2 + H_2O \qquad (4)$$
$$CuO + H_2 \rightarrow Cu + H_2O \qquad (5)$$
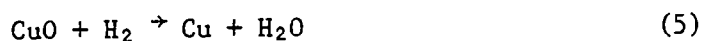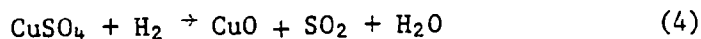
The $SO_2$ produced by the regeneration of the reactor can be further processed to recover the sulfur as sulfuric acid or elemental sulfur.

The SFGT pilot plant processed a 1000 scfm slipstream of flue gas which was withdrawn between the economizer and the air preheater of the coal-fired unit 2 at Tampa Electric Company's Big Bend Station. Flue gas from the boiler contained full particulate loading and was heated by in-line burners before entering the reactor. Flue gas flowed up through the reactor during acceptance of $SO_2$ and bypassed the reactor during the regeneration of the acceptor. During the program, some tests were conducted in which the reactor was fully loaded with $SO_2$ and $NO_x$ was the only pollutant removed. While these tests were conducted, the reactor processed flue gas continuously. During cyclic operation, the acceptance period ranged from 50 to 70 minutes, with an average of 65 minutes, while the regeneration period ranged from 22 to 40 minutes, with an average of 29 minutes.

Figure 2 is a schematic of the SFGT pilot plant which shows the location of the sampling ports used during the test program. Flue gas temperature was approximately 400 °C at both the inlet and outlet sampling ports. Full particulate loadings were present at both sampling locations.
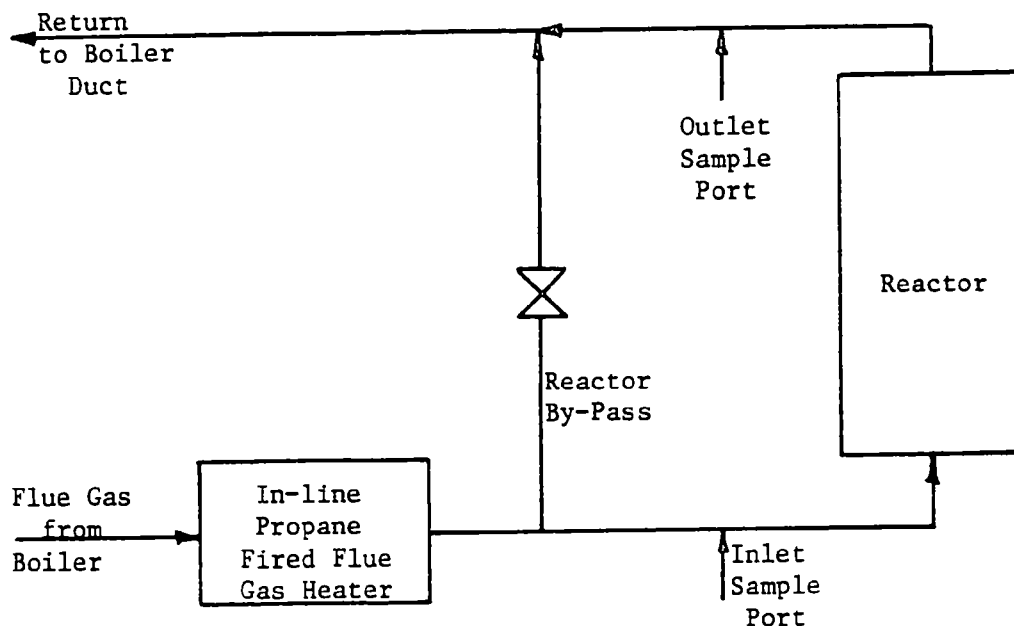


Figure 2. Schematic of the SFGT pilot plant.

# SECTION 4

## RESULTS

The stack sampling program was conducted by Radian during the period June through August, 1980. A mobile laboratory was used during the program and most of the analytical work was completed on-site. The results of the stack sampling work are summarized in Tables 1 and 2 which show inlet and outlet concentrations of the species measured at the HZ and SFGT pilot plants respectively. It should be noted that no results for $N_2O$ are presented due to the fact that the measuring technique proved unsatisfactory.

As shown in Table 1, the concentrations of CO, HC, HCN and nitrosoamines at the HZ pilot plant were all below the detection limit of the techniques used. This indicates that no significant change in the concentrations of these species occurred in the reactor. Table 1 does show significant increases in the concentrations of $NH_3$ and $SO_3$ emitted from the reactor, while the apparent change in particulate loading is believed to be the result of random error or unaccounted for stratification in the ducts.

Table 2 shows the results from the sampling program of the SFGT unit. Concentrations of HCN and nitrosoamines were below the detection limit, again showing that no significant change in the concentration of these species occurred in the reactor. Decreases in both the HC and CO concentrations were measured across the reactor. This change is probably due to oxidation of these pollutants across the reactor. It is believed that the relatively high levels of CO and HC's measured were due to emissions from the in-line propane burners located upstream of the reactor. As shown, a decrease in $SO_3$ concentration was also measured across the reactor. This decrease is due to removal of $SO_3$ from the flue gas via reaction with the acceptor. The apparent change

TABLE 1 - STACK SAMPLING RESULTS AT HZ PILOT UNIT

| Flue Gas Component | Reactor Inlet Concentration[1] | Reactor Outlet Concentration[1] | Measurement Technique |
|---|---|---|---|
| Nitrosoamines[2] | <5 µg/dscm | <5 µg/dscm | Absorption, Extraction, Gas Chromatograph w/nitrogen specific detector |
| Hydrogen Cyanide[2] | <.01 mg/dscm | <.01 mg/dscm | Absorption, distillation, titration |
| Ammonia | Not measured | 54.8 ppmv (dry basis) | Absorption, distillation, titration |
| Sulfur Trioxide | 8.4 ppmv (dry basis) | 20.7 ppmv (dry basis) | Controlled Condensation, Ion Chromatograph |
| Hydrocarbons[2] $(C_1-C_6)$ | <1.0 ppmv | <1.0 ppmv | Gas Chromatograph Flame Ionization Detector |
| Carbon Monoxide[2] | <0.017% | <0.017% | Fischer Gas Partitioner |
| Particulate Loading | 7.1 gm/dscm | 7.7 gm/dscm | In stack filter |

[1]Average of 3 or more tests

[2]Below the detection limit

TABLE 2 - STACK SAMPLING RESULTS AT UOP PILOT PLANT

| Flue Gas Component | Reactor Inlet Concentration[1] | Reactor Outlet Concentration[1] | Measurement Technique |
|---|---|---|---|
| Nitrosoamines[4] | <5 μg/dscm | <5 μg/dscm | Absorption, Extraction, Gas Chromatograph w/nitrogen specific detector |
| Cyanides[4] | <.01 mg/dscm | <.01 mg/dscm | Absorption, distillation, titration |
| Ammonia | Not measured | 15.3 ppmv (dry basis)[2] 49.0 ppmv (dry basis)[3] | Absorption, distillation, titration |
| Sulfur Trioxide | 11.4 ppmv (dry basis) | 0.1 ppmv (dry basis) | Controlled condensation, ion chromatograph |
| Hydrocarbons $(C_1-C_6)$ | 28.5 ppmv | 21.0 ppmv | Gas Chromatograph Flame Ionization Detector |
| Carbon Monoxide | 0.13% | <0.017%[4] | Fischer Gas Partitioner |
| Particulates | 8.9 gm/dscm | 6.3 | In stack filter |

[1]Average of 2 or more tests

[2]During simultaneous $SO_x/NO_x$ removal tests

[3]During $NO_x$ removal only tests

[4]Below the detection limit

in particulate concentration is believed to be due to unaccounted for stratification in the ducts.

The following discussion examines the stack sampling results in more detail. In addition, a brief discussion of the analytical techniques are presented.

Ammonia

Ammonia samples were collected at the reactor outlet at both the HZ and SFGT pilot plants. At the SFGT pilot plant, samples were collected during both cyclic and $NO_x$ only operation. The samples collected during cyclic operation were taken over the course of an entire cycle yielding an average $NH_3$ concentration at the reactor outlet during the cycle.

Ammonia emission samples were collected by filtering the flue gas in the duct and drawing the sample through a glass-lined probe into two impingers containing 5 wt percent $H_2SO_4$. A composite sample was produced by combining the two impinger solutions with the washings from the sample probe. A 250 ml aliquot of the composite was taken for analysis of $NH_3$ nitrogen by a distillation/titration procedure. The aliquot was buffered with a sodium borate buffer solution, and the pH adjusted to 9.5 using sodium hydroxide. This mixture was then distilled for approximately one hour, until more than 200 ml of distillate was collected. The distillate was captured subsurface in a boric acid indicating solution. This product solution was then titrated with a standard .02 N sulfuric acid titrant.

The results of the $NH_3$ emissions sampling at the HZ pilot plant are presented in Table 3. As shown, the $NH_3$ emissions were quite high, averaging about 55 ppm for all the tests. This emission rate is much higher than the expected rate of 10 to 20 ppm, and it could have serious impacts on equipment located downstream of the SCR process. In addition, $NH_3$ emissions of 50 ppm could result in formation of an ammonium sulfite/bisalfite plume downstream

## TABLE 3 - HITACHI-ZOSEN/CHEMICO PILOT PLANT NH$_3$ EMISSIONS

| Date | Time | NO$_x$ In (ppm wet) | NH$_3$:NO$_x$ | NH$_3$ Emission (ppm dry) |
|------|------|---------------------|---------------|----------------------------|
| 7-18 | 13:45 - 14:05 | 459 | 0.91 | 45 |
| 7-18 | 15:11 - 15:31 | 451 | 0.97 | 46 |
| 7-29 | 14:54 - 15:20 | 466 | 0.92 | 49 |
| 7-30 | 10:37 - 10:57 | 453 | 0.92 | 60 |
| 8-1  | 12:23 - 12:48 | 469 | 0.99 | 44 |
| 8-2  | 11:17 - 11:42 | 479 | 0.99 | 63 |
| 8-2  | 18:50 - 19:10 | 440 | 1.05 | 54 |
| 8-5  | 15:29 - 15:57 | 450 | 0.89 | 58 |
| 8-6  | 16:53 - 17:13 | 460 | 1.01 | 74* |
| 8-7  | 11:17 - 11:42 | 493 | 0.89 | 41* |
| 8-7  | 13:15 - 13:40 | 482 | 0.98 | 68* |

*Note:  Sample analyzed by pH adjustment, direct nesslerization/spectrophotometry instead of pH adjustment, distillation/titration as for other samples.  Tests from 7-29 and 8-1 were run with both methods with good agreement.

of a wet FGD system. The reason for the high $NH_3$ emission rate is unclear at this time, but is probably due to an inadequate amount of catalyst in the reactor. Other possibilities, such as a high $NH_3$ injection rate have been checked and do not explain the measured $NH_3$ emission rate.

The results of the $NH_3$ measurements at UOP are presented in Table 4. As shown, the samples taken during the $NO_x$ only tests indicate an average $NH_3$ emission rate of 49 ppm which is quite similar to the results from the HZ $NH_3$ emission tests. The samples collected during the cyclic operation of the SFGT process exhibit results which are quite different from the non-cyclic operation. Samples collected during cyclic operation show an average $NH_3$ concentration of about 15 ppm in the gas exiting the reactor. This emission rate is more in line with expectations prior to the start of the pilot scale tests, and should not present serious problems downstream of the SCR reactor. It should be noted, however, that the measured $NH_3$ concentration is an average over the acceptance period and no information is available on the instantaneous $NH_3$ emission rate over the course of a cycle.

Currently, no explanation has been found for the marked difference in $NH_3$ emission rates during cyclic and non-cyclic operation at essentially the same operating conditions (i.e., flue gas flow, temperature, $NH_3$ injection rate). One possibility is that $Cu$ and $CuO$ promote $NH_3$ oxidation at a higher rate than $CuSO_4$ does. Another possibility is that the metal surfaces in the reactor strongly adsorb $NH_3$. During non-cyclic operation this adsorption would occur only once and the surfaces would quickly become saturated with $NH_3$. During cyclic operation $NH_3$ would be desorbed during regeneration. Consequently, the reactor internals would always have some capacity for adsorbing $NH_3$, thus lowering the $NH_3$ emission rate during acceptance.

## TABLE 4 - SFGT PILOT PLANT $NH_3$ EMISSIONS

| Date | Time | UOP Cycle # | $NO_x$ In (ppm dry) | $NH_3:NO_x$ | $NH_3$ Emissions (ppm dry) |
|------|------|-------------|---------------------|-------------|----------------------------|
| 6-21 | 16:12 - 17:12 | 875 | 380 | 1.17 | 15 |
| 6-23 | 12:49 - 13:52 | 903 | 420 | 1.21 | 16 |
| 6-24 | 13:26 - 14:36 | 918 | 390 | 1.31 | 22 |
| 6-26 | 13:23 - 14:20 | 948 | 375 | 1.25 | 17 |
| 6-26 | 17:52 - 18:48 | 951 | No UOP Data | | 16 |
| 6-27 | 15:06 - 16:02 | 965 | No UOP Data | | 11 |
| 6-28 | 15:49 - 16:52 | 982 | 392 | 1.17 | 12 |
| 6-28 | 17:27 - 18:32 | 983 | 402 | 1.19 | 13 |
| 6-30 | 15:27 - 17:06 | 1004 | No UOP Data | | 16 |
| 7-11 | 14:01 - 14:23 | $NO_x$ Only | 420 | 1.18 | 47 |
| 7-15 | 14:50 - 15:15 | $NO_x$ Only | 327 | 1.21 | 52 |
| 7-15 | 18:28 - 18:53 | $NO_x$ Only | 224 | 1.38 | 48 |

TABLE 5 - CHANGE IN $SO_3$ CONCENTRATION ACROSS THE REACTOR IN THE HZ PROCESS

| Date | Time | $SO_3$ Inlet (ppm dry) | $SO_3$ Outlet (ppm dry) | $SO_2$ Oxidation (%) |
|------|------|------|------|------|
| 7-23 | 16:30 - 17:20 | 11.0 | 25.3 | 1.5 |
| 7-24 | 16:50 - 17:40 | 7.5 | 14.8 | 1.1 |
| 7-25 | 16:25 - 17:10 | 6.6 | 21.9 | 1.9 |

TABLE 6 - CHANGE IN $SO_3$ CONCENTRATION ACROSS THE REACTOR IN THE SFGT PROCESS

| Date | Time | $SO_3$ Inlet (ppm dry) | $SO_3$ Outlet (ppm dry) | Removal (%) |
|------|------|------|------|------|
| 10-8 | 14:40 - 15:40 | 10.4 | 0.095 | 99.1 |
| 10-8 | 17:15 - 18:45 | 12.4 | 0.108 | 99.1 |

## Sulfur Trioxide

Sulfur trioxide was collected using a controlled condensation system. The $SO_3$ was selectively condensed at 80°C in a modified Graham condenser. The sample was recovered by rinsing the condenser coil with deionized water and the sulfate concentration of the coil rinse was measured by ion chromatagraphy. The results of the $SO_3$ sampling are presented in Tables 5 and 6.

For the three test results from the HZ pilot plant, shown in Table 5, an average of 1.5 percent of the inlet $SO_2$ is oxidized to $SO_3$ across the reactor. This effect is to be expected since a primary component of the catalyst, vanadium pentoxide, is used commercially as a $SO_2$ oxidation catalyst. The increase in $SO_3$ concentration, by an average of 12.3 ppm, has potentially important downstream impacts. First, the resultant higher sulfuric acid ($H_2SO_4$) dewpoint decreases the amount of heat that a boiler air preheater can safely extract from the flue gas without suffering increased corrosion. This can be a significant energy penalty. Increased maintenance costs and decreased service life for the preheater or downstream equipment, due to $H_2SO_4$ attack could result. Another potential impact is an increase in ammonium bisulfate ($NH_4HSO_4$) formation in the preheater from the reaction of $SO_3$ and water with residual ammonia exiting the SCR reactor. This can result in an increased pressure drop for the system. Maintenance costs could increase due to more frequent cleaning of the preheater. Finally, any additional $SO_3$ that passed through the preheater would most likely result in increased $H_2SO_4$ emissions. Conventional flue gas desulfurization (FGD) systems are not very effective for capturing the $H_2SO_4$ aerosols or mist that would form.

For the two tests run at UOP's plant, an average of 99% of the $SO_3$ was removed from the flue gas. This $SO_3$ removal capability of the system is also important. By lowering the $H_2SO_4$ dewpoint, it may be possible to

operate the air preheater at a lower flue gas exit temperature and thus recover more energy in the preheater. This can be a significant energy savings. Lower $SO_3$ concentrations should minimize downstream impacts, decreasing emissions and maintenance and increasing equipment life.

## Particulates

Particulates were collected by filtering the flue gas in stack (EPA Reference Method 17) with a 30 by 100 mm glass fiber sampling thimble. Traverses of the duct were conducted to ensure a representative sample. The samples were collected isokinetically in accordance with established EPA methods. The samples were weighed to determine grain loadings and a composite of three samples was analyzed to determine the elemental composition of the particulates.

The results of the particulate loading measurements are presented in Tables 7 and 8. At the HZ pilot plant, the grain loading averaged 7.1 gm/dscm at the inlet and 7.7 gm/dscm at the outlet. No particulate matter is produced within the system, so the 8% difference in grain loading values is probably attributable to small random errors. It is also possible that stratification of the particulates existed in the ducts, since the sample ports were located close to downstream disturbances.

At the SFGT plant, the grain loading averaged 8.9 gm/dscm at the inlet and 6.3 gm/dscm at the outlet. No large air leaks are present in the system to dilute the flue gas, so the 29% difference in grain loading values is due to an error in sampling. The magnitude of the difference suggests a systematic error in the sampling procedure. Because of the location of sample ports on the SFGT pilot unit, it was only possible to traverse the duct in a single plane. Since the sample ports were also located close to disturbances at the SFGT plant, it is conceivable that

TABLE 7 - GRAIN LOADINGS MEASURED AT THE HZ PILOT PLANT

| Date | Time | Inlet (gm/dscm) | Outlet (gm/dscm) |
|------|------|-----------------|-------------------|
| 7-29 | 17:50 - 18:50 | 7.5 | 7.8 |
| 7-30 | 17:02 - 18:02 | 6.9 | 8.4 |
| 7-31 | 14:09 - 15:09 | 6.9 | - |
| 7-31 | 18:08 - 19:08 | - | 6.9 |

TABLE 8 - GRAIN LOADINGS MEASURED AT SFGT PILOT PLANT

| Date | Time | Inlet (gm/dscf) | Outlet (gm/dscf) |
|------|------|-----------------|-------------------|
| 6-19 | 10:47 - 11:27 | 8.3 | 6.7 |
| 6-19 | 13:55 - 14:35 | 11.2 | 6.8 |
| 6-19 | 17:05 - 17:45 | 7.4 | 5.5 |

representative sampling of the duct was not possible using this single plane.

Table 9 presents the results of the elemental analysis of the particulates collected at the HZ pilot plant. This analysis was conducted to determine if catalyst erosion was causing an increase in the concentration of Vandium (V) or Titanium (Ti) in the particulates leaving the reactor. As shown in Table 9, an apparent increase in all elements occurs across the reactor, but the relative concentrations on V and Ti remain constant. This indicates that there is no measurable change in the concentration of V or Ti in the particulates exiting the reactor. The apparent change could be due to several factors. One possibility is the presence of an inert material (e.g., unburned carbon) in the inlet sample. This material may have entered the sample due to contamination, or if it is indeed unburned carbon, it may have been burned in the flue gas heater located between the reactor inlet and outlet sample ports. In any event, it can be concluded that no significant increase in the concentrations of V or Ti in the particulates occurred due to catalyst erosion.

Table 10 presents the results of the elemental analysis of the particulates collected at the SFGT pilot plant. At this plant, the elements of interest are Alumina (Al) and Copper (Cu). As shown, no significant change in the composition of the particulates was measured with respect to these elements. The changes which are shown in Table 10 are probably due to random errors in the sampling on analysis technique and are not representative of real changes in particulate composition. Therefore, it can be concluded that no significant increase in the concentrations of Al or Cu in the particulates occurred due to catalyst erosion.

Carbon Monoxide and Hydrocarbons

Samples were collected by cooling a filtered flue gas stream to about 200°F and then passing it through a Perma-Pure dryer to remove moisture. Samples were collected in Mylar gas bags that had been purged several times with the conditioned gas.

TABLE 9 - RESULTS OF PARTICULATE ANALYSIS AT THE HZ PILOT PLANT

| Component[1] | In | Out | Out/In |
|---|---|---|---|
| Al | 10.7% | 13.0% | 1.21 |
| Ca | 8200 ppm | 9900 ppm | 1.21 |
| Fe | 4.9% | 6.0% | 1.22 |
| K | 2.0% | 2.5% | 1.25 |
| Mg | 6300 ppm | 7800 ppm | 1.24 |
| Mn | 190 ppm | 240 ppm | 1.26 |
| Sn | 490 ppm | 680 ppm | 1.40 |
| Na | 4200 ppm | 4700 ppm | 1.12 |
| Si | 18% | 23% | 1.28 |
| Zn | 190 ppm | 250 ppm | 1.32 |
| Cu | 150 ppm | 170 ppm | 1.13 |
| Ti | 5800 ppm | 6900 ppm | 1.19 |
| V | 270 ppm | 330 ppm | 1.22 |

[1]Concentrations are on a mass fraction basis

TABLE 10 - RESULTS OF PARTICULATE ANALYSIS AT THE SFGT PILOT PLANT

| Component[1] | In | Out | Out/In |
|---|---|---|---|
| Al | 8.6% | 8.0% | .93 |
| Ca | 1.8% | 1.8% | 1.00 |
| Fe | 12% | 11.1% | 0.93 |
| K | 1.5% | 1.4% | 0.93 |
| Mg | 5100 ppm | 5000 ppm | 0.98 |
| Mn | 300 ppm | 320 ppm | 1.07 |
| Sn | 270 ppm | 270 ppm | 1.00 |
| Na | 4300 ppm | 5100 ppm | 1.19 |
| Si | 20% | 16% | 0.80 |
| Zn | 410 ppm | 720 ppm | 1.76 |
| Cu | 96 ppm | 100 ppm | 1.04 |
| Ti | 5400 ppm | 5100 ppm | 0.94 |
| V | 255 ppm | 340 ppm | 1.33 |

[1]Concentrations are on a mass fraction basis

The samples were analyzed on-site using a Fisher Gas Partioner Model 1200 TCD-GC and an AID portable Gas Chromatograph. The gas samples were introduced into the instruments, and the retention times and peak heights were compared to those obtained from mixes of standard gases. At the HZ pilot plant the GC became inoperative and $C_1-C_6$ hydrocarbon samples were collected in snout* bags and transported to Radian's Austin Laboratories where they were analyzed within a week of collection on a Tracor Model 560 FID-CG. The results are presented in Tables 11 and 12.

As shown in Table 11, the concentration of both CO and HC's at the HZ pilot plant were below the detection limit of the analysis techniques so no conclusion could be drawn concerning the impact of the catalyst on these pollutants. However, at the SFGT pilot plant, decreases in the concentrations of both CO and HC were measured across the reactor. This decrease is attributed to oxidation of the CO and HC's by the catalyst forming $CO_2$ and $H_2O$. The oxidation of these compounds was not unexpected since the $NO_x$ reduction reaction is actually an oxidation of $NH_3$ by $NO_x$ and the catalyst is basically an oxidation catalyst. It should be noted that the high levels of CO and HC's at the SFGT pilot plant were probably a result of incomplete combustion in the propane burners used for flue gas temperature control upstream of the reactor.

Hydrogen Cyanide (HCN)

Cyanide samples were collected by bubbling filtered flue gas through a 10% sodium hydroxide solution. Samples were shipped to Radian's Austin Laboratories for analysis. It was originally proposed to measure the concentration of cyanide spectrophotometrically with a pyridine-barbituric

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*Consists of layers of polyester, polyvinyl chloride, aluminum, polyamide and polyethylene.

TABLE 11 - FISHER GAS PARTIONER AND G.C. DATA FROM THE HZ PILOT PLANT

| Sampling Location | Species (as % of total flue gas) | | | | |
|---|---|---|---|---|---|
| | $CO_2$ | $O_2$ | $N_2$ | CO | $C_1-C_6$ |
| Inlet | 17.8 | 4.4 | 69.7 | <0.017 | <1 ppm |
| Outlet | 17.2 | 4.9 | 68.5 | <0.017 | <1 ppm |

TABLE 12 - FISHER GAS PARTIONER AND G.C. DATA FROM THE SFGT PILOT PLANT

| Sampling Location | Species (as % of total flue gas) | | | | |
|---|---|---|---|---|---|
| | $CO_2$ | $O_2$ | $N_2$ | CO | $CH_4$ |
| Inlet | 17.5 | 4.8 | 70.5 | 0.13 | 28.4 ppm |
| Outlet | 17.6 | 4.8 | 70.3 | <0.017 | 21.0 ppm |

The total $C_1-C_6$ hydrocarbon concentration was the same as the $CH_4$ concentration.

acid reagent, but this method proved to be unfeasible due to inferference from $SO_2$ absorbed in the sodium hydroxide solution. A silver nitrate $(AgNO_3)$ titration method was used instead. The silver ions complex with the cyanide to form $Ag(CN^-)_2$. The excess $Ag^+$ is detected by paradimethylamino-benzalrhodanine, which undergoes a yellow to salmon color change in the presence of $Ag^+$ ions.

The $AgNO_3$ titrametic method employed by Radian could detect cyanide at a level equal to or greater than 0.01 mg/dscm. The concentration of cyanide at Chemico and UOP pilot plants was below this limit of detection at both the inlet and outlet sampling ports. This indicates that no significant increase in the flue gas HCN concentration occurs across the reactor at either pilot plant.

## Nitrosoamines

Nitrosoamine samples were collected by bubbling filtered flue gas through a 1N potassium hydroxide solution. The samples were packed in ice and shipped to Radian's Austin laboratories. There each sample was serially extracted with distilled-in-glass methylene chloride to remove the organic species from the sample matrix. The methylene chloride extracts were then combined and concentrated by evaporation to less than 10 ml. Hexane (10 ml) was added and each extract was reconcentrated to remove the methylene chloride. The resulting hexane extracts were then analyzed by GC.

The samples were initially analyzed by a nitrogen specific detector. The chromatogrphic data was generated using a 6' x 4mm 10 percent carbowax 20M + two percent KOH column. Two separate injections were conducted for each sample. The first injection at 110°C isothermal was employed for low molecular weight nitrosoamines such as N-nitrosodimethylamine. A second injection at 220°C isothermal was employed for higher boiling species such as N-nitrosodiphenylamine. Several small peaks were observed; none of these matched the retention time of known nitrosoamines in the standard used. The

samples were then analyzed by a Hall electroconductivity detector operated in the nitrosoamine specific mode using a 8' x 2 mm 15 percent LAC-2R-446 Column at 145° isothermal. No peaks were observed in these analyses.

The GC/MS analysis could detect nitrosoamines at a level equal to or greater than 5 ug/dscm. The concentration of nitrosoamines at the Chemico and UOP pilot plants was below this limit of detection at both the inlet and outlet sampling ports. This shows that no significant change in nitrosoamine concentrations occurred across the reactor at either pilot plant.

## Nitrous Oxide ($N_2O$)

Grab samples of flue gas were collected in Mylar bags. The gas was cooled and filtered to remove condensed ammonium salts and water vapor. The samples were then injected into a Miran 1A Gas Analyzer (Wilks Scientific Corporation) and the concentration of $N_2O$ was determined by infra red (IR) spectral analysis.

Nitrous oxide is not normally measured in flue gas studies and there is no generally accepted procedure. The method used in the sampling program was not sensitive enough to detect the presence of $N_2O$. Several interfering peaks combined with the low level of any $N_2O$ present made determination of the $N_2O$ concentration impossible.

In order to measure $N_2O$, it would have been necessary to concentrate it prior to analysis. One technique which has been used for measuring low $N_2O$ levels is cryogenic trapping and gas chromatography. A silica gel column is used to concentrate the $N_2O$ in the gas sample. After withdrawal from the duct, particulates, water, and $CO_2$ are successively removed from the sample. The gas is then passed through a gel-concentration column maintained at $-70°C$ which further concentrates the $N_2O$. The $N_2O$ is desorbed by flushing with helium. The gas sample passes through a separation column and the $N_2O$

concentration is measured with a thermal conductivity detector.

This method is routinely used to measure atmospheric level of $N_2O$ (250-300 ppb), but can detect levels down to at least 50 ppb.

## SUMMARY

The stack sampling program conducted by Radian was designed to quantify changes in the emission rate of secondary pollutants from the SCR process. The results of this program showed that:

- A significant quantity of $NH_3$ is emitted from the HZ process and from the SFGT process during non-cyclic ($NO_x$ only) operation,

- The HZ process produces $SO_3$ by oxidation of $SO_2$ at a rate equivalent to 1 to 2 percent of the $SO_2$ in the flue gas.

- The SFGT process removes nearly all the $SO_3$ in the flue gas entering the reactor. This could have a beneficial impact on downstream equipment which may be subject to acid corrosion.

- The particulate loadings in the processed flue gas at both pilot plants was about 7 gm/dscm which is typical of many coal-fired applications.

- No significant change in particulate composition was measured across the reactor at either pilot unit.

- The concentrations of both CO and HC's were reduced across the SFGT reactor. It is believed this reduction was due to oxidation. No change was measured in the concentration of CO or HC's at the HZ pilot unit due to the fact the concentrations were below the detection limit of the analytical techniques.

- No significant change in the concentrations of HCN or nitrosoamines occurred at either pilot unit.

- The technique used for measuring $N_2O$ proved unsatisfactory for the quantity of $N_2O$ (if any) present in the flue gas at either pilot unit.

Appendix C


TECHNICAL NOTE


RESULTS OF THE CONTINUOUS MONITOR
CERTIFICATION TESTS AT THE
EPA SPONSORED NO$_x$ PILOT PLANTS


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# SECTION 1

## INTRODUCTION


The Environmental Protection Agency sponsored pilot scale tests of two selective catalytic reduction (SCR) processes for $NO_x$ removal. The processes tested were the Hitachi-Zosen (HZ) process and the Shell flue gas treatment (SFGT) process which also removes $SO_2$. The contractors responsible for design and operation of these pilot units were Chemico Air Pollution Control Corporation (HZ process) and the Process Division of UOP (SFGT process). In both cases, these contractors were responsible for collection, evaluation, and reporting of test data.

As part of the pilot scale test program, EPA contracted Radian Corporation to conduct an independent evaluation of the performance of both pilot units. This independent evaluation consisted of several steps including:

- A quality assurance program to check measurements being made by the process operators,

- A sampling program to quantify changes in secondary process emissions across the SCR reactors, and

- A program to certify the performance of the continuous $NO_x$ monitors (and $SO_2$ monitors at the SFGT pilot unit) using EPA reference methods.

This technical note presents the results of certification tests to assure the accuracy of the data collected by the continuous $NO_x$ and $SO_2$ monitors. Results of the secondary emissions sampling program and the quality assurance program are contained in separate technical notes.

# SECTION 2

## OBJECTIVE AND APPROACH

The objective of the continuous monitor certification tests was to insure the accuracy of the data generated by the continuous monitors at the two pilot plants. In conjunction with the quality assurance program, the certification tests were expected to provide accurate characterization of the pilot plant's performance permitting the data collected by Chemico and UOP to be used as a basis for a more detailed process evaluation.

The approach used in conducting the continuous monitor certification tests was based on a formal procedure which has been developed by EPA to insure the accuracy of monitors measuring emissions from sources which must comply with new source performance standard emission limitations. According to the procedure developed by EPA, a continuous emission monitor must pass a number of performance tests in order to be certified. These tests include:

- calibration error,

- response time,

- 2- and 24-hour zero drift,

- 2- and 24-hour calibration drift, and

- relative accuracy.

The performance specifications for each of the above certification tests are shown in Table 1. These specifications are those contained in the Federal Register, Vol. 44, No. 197, Wednesday, October 10, 1979 - "Proposed Rules: Standards of Performance for New Stationary Sources; Continuous Monitoring Performance Specifications".

TABLE 1. CONTINUOUS MONITORING SYSTEM PERFORMANCE
AND EQUIPMENT SPECIFICATIONS

| Certification Test | Performance Specification |
|---|---|
| Calibration Error | $\leq$ 5 percent for mid-range and high level calibration values |
| Response Time | $\leq$ 15 minutes |
| Zero Drift (2-hour) | $\leq$ 2 percent of Span[1] value |
| Zero Drift (24-hour) | $\leq$ 2.5 percent of Span[1] value |
| Calibration Drift (2-hour) | $\leq$ 2 percent of Span[1] value |
| Calibration Drift (24-hour) | $\leq$ 2.5 percent of Span[1] value |
| Relative Accuracy | $\leq$ 20 percent of reference test data in terms of emission standard[2] or 10 percent of the applicable standard, whichever is greater |

[1]Span refers to the range of the emission monitor (e.g., 0-500 ppm).
[2]Emission standards are expressed in terms of pollutant mass emissions per unit of heat input.

Because the pilot plants were operated as experimental systems, the operating characteristics of the continuous monitors were different than those of a continuous monitor system for a typical commercial scale application. In particular, the pilot plant continuous monitors received considerably more operator attention in an effort to insure the quality of the data being collected. As a consequence, not all the continuous monitor performance specifications were strictly adhered to. The major emphasis of the certification tests conducted at the pilot plants was to insure the relative accuracy of the continuous monitors. The other certification tests were considered of secondary importance.

The following discussion presents the procedure for conducting each certification test, identifies areas where the certification tests at the pilot plants differed from those outlined in the performance specifications, and presents reasons for the differences. The certification results are presented in detail in Section 3. For more details of the certification test procedures, the reader is referred to the Federal Register mentioned above.

## Calibration Error

Calibration error is a measure of the ability of a continuous monitor to accurately analyze the concentration of a calibration gas. To determine calibration error, a series of 15 measurements are made; 5 each of high and mid-level calibration gas concentrations and 5 of zero gas (air). The measurements are made such that the same gas concentration is not measured two or more times in a row (i.e., non-consecutively). The calibration error is then determined by the difference between the concentration of the calibration gas (which has been verified by one of several techniques defined in the CEM performance specifications) and the continuous monitor readings. Specifically the error is defined by Equation 1.

$$\text{Calibration Error} = \frac{|\bar{X}| + |CI_{95}|}{RV} \qquad (1)$$

where $|\bar{X}|$ = absolute value of the mean difference between the monitor reading and the calibration gas concentration.

$RV$ = concentration of the calibration gas.

$|CI_{95}|$ = absolute value of the 95 percent confidence interval which is defined by Equation 2.

$$CI_{95} = \frac{t_{.975}}{n(n-1)^{\frac{1}{2}}} \left( n \sum X_i^2 - \left( \sum X_i \right)^2 \right)^{\frac{1}{2}} \qquad (2)$$

where $n$ = the number of measurements (in this case 5)

$t$ = 2.776 (for 5 measurements)

$X_i$ = difference between the continuous monitor reading and the calibration gas concentration for individual readings.

For the continuous monitor to pass the calibration error test, the error as defined by Equation 1 must be less than or equal to 5 percent for both the mid- and high-range calibration gases. There was no deviation from this procedure in conducting the calibration error test at either pilot plant.

## Response Time

Response time is a measure of the time which elapses before a continuous monitor responds to a change in the pollutant concentration in a duct. To determine response time, zero gas is introduced into the continuous monitor's sampling system at the duct/sample line interface. Once the monitor reading stabilizes at zero, the sampling system is switched from zero gas to monitoring the stack effluent and the time required for the monitor to reach a stable reading is determined. This is the upscale response time. Subsequently, the downscale response time is determined by introducing high-level calibration gas into the continuous monitor sampling system at the duct/sample line interface. Once the monitor's reading stabilizes at the high level gas concentration, stack gas is introduced into the sample line and the time required for the monitor's reading to reach a stable value downscale is determined. This procedure is repeated three times and the mean upscale and downscale response times are determined. The maximum of these values must be less than 15 minutes for the continuous monitor to pass this test.

This method of measuring response time represents a slight change from previous EPA performance specifications which were the ones followed during the certification tests at the pilot plants. In the previous certification procedures, response time was determined by alternately introducing zero and high-level calibration gas into the sample line at the duct/sample line interface. Upscale response time was that required to stabilize the CEM system reading after the switch from air to high-level calibration gas while downscale response time was measured in the opposite manner. This measure of response time should provide an accurate indication of system response provided care is taken to prevent excessive span gas pressure in the sample line.

## Zero and Calibration Drift

Zero and calibration drift are measures of how the continuous monitor's response to zero and calibration gases change with time. To measure two-hour drift, zero and high level calibration gases are introduced into the instrument at two-hour intervals. The differences between the monitor readings and

the zero or calibration gas concentrations are recorded and a total of 15 sets of data are collected. Drift is then calculated using Equations 1 and 2 where the reference value (RV) equals the range of the continuous monitor and $t_{.975}=2.145$ (for 15 tests). 24-hour drift is measured in a similar manner. At the start of a 24-hour period the monitor is calibrated and zeroed and then no further adjustments are made. After 24 hours, zero and calibration drift are recorded and the instrument is recalibrated. A total of 7 measurements are required to determine 24-hour drift and Equations 1 and 2 are used. For 7 measurements, $t_{.975}=2.447$.

Because the pilot plants were operated as experimental units, the accuracy of continuous monitors was of particular concern. As a consequence, the calibration and zero settings on the continuous monitors were adjusted about once per hour for the SFGT pilot plant (generally at the start and completion of an acceptance period), and every two hours at the HZ pilot plant. Obviously, the 24-hour drift test is not meaningful under these circumstances and, in the case of the SFGT pilot plant, the two-hour drift test could not be completed strictly according to performance specifications. Instead, the zero and calibration drift was determined for the period between initial and final calibration and zeroing of a monitor.

### Relative Accuracy

Relative accuracy is the most important test in determining the performance of the continuous monitors. This test is comparison of the continuous monitor's analysis of stack gas with a stack gas analysis as determined by EPA reference methods (Method 3 for $O_2$ and $CO_2$, Method 6 for $SO_2$, and Method 7 for $NO_x$). Relative accuracy is determined by making a minimum of 9 reference method tests (for Method 7, one test requires three samples) and comparing the results to the continuous monitor readings during the time the reference tests were collected. In addition, for determining the relative accuracy of $NO_x$ and $SO_2$ continuous monitors, simultaneous reference method tests for $O_2$ are required so the $NO_x$ and $SO_2$ concentrations can be converted to a mass emissions per unit of heat input (e.g., $lb/10^6$ Btu) basis.

After the reference method tests are completed and the continuous monitor and reference method test results are converted from concentrations to a mass emission per unit heat input basis, the relative accuracy can be determined. Relative accuracy is calculated using Equations 1 and 2 where the reference value (RV) is equal to the mean of the reference method tests and $t_{.975}=2.306$ (for 9 tests).

This procedure was followed exactly at the HZ pilot plant. And 9 sets of reference method tests for both $SO_2$ and $NO_x$ were completed at the inlet and outlet of the SFGT pilot plant reactor. However, reference method tests for $O_2$ or $CO_2$ were not included because UOP did not operate a diluent monitor. As a result, the CEM data could not be converted to a mass emission per unit of heat input basis. In the case of the SFGT pilot plant this does not impact the validity of the relative accuracy tests because: (1) the reactor operated under 7.5 kPa (30 in $H_2O$) pressure so no dilution occurred between the reactor inlet and outlet, and (2) the measurements made by the continuous monitors were intended to demonstrate the ability of the process to achieve a specific percentage reduction in $NO_x$ and $SO_2$ emissions based on pollutant concentrations rather than a reduction in emissions below a specific mass emission rate per unit heat input.

# SECTION 3

## CONTINUOUS MONITOR CERTIFICATION TEST RESULTS

The certification tests conducted at the HZ and SFGT pilot plants were discussed in Section 2 of this technical note. This section presents a summary and individual results from the certification tests. It also includes the results of reference method tests on the calibration gases used during the certification test program.

### Summary

Table 2 summarizes the results of the continuous monitor certification tests for both the HZ and SFGT pilot plants. As shown, the test results for all the continuous monitors met the performance specifications with one exception; the relative accuracy of the outlet $NO_x$ monitor at the SFGT pilot plant was over 50 percent while the performance specifications require a relative accuracy of 20 percent or less. These data indicate that, with the exception of the SFGT outlet $NO_x$ analyzer, the continuous monitors were making accurate measurements of flue gas $NO_x$ and $SO_2$ concentrations. It should be noted that 24-hour zero and calibration tests were not included in the certification tests since the instruments were calibrated at least every two hours, thus making the 24-hour drift tests meaningless. In addition, at the SFGT plant, only one $SO_2$ monitor was used, so the values for all tests except response time and relative accuracy are identical.

The poor relative accuracy of the outlet $NO_x$ analyzer shown in Table 2 would tend to indicate that the monitor was making inaccurate measurements of flue gas $NO_x$ concentrations. However, there are several factors which must be considered when evaluating these test results. First, the absolute error in

## TABLE 2. CONTINUOUS MONITOR CERTIFICATION TEST RESULTS

| Certification Test | Performance Specification | SFGT Pilot Plant | | | | HZ Pilot Plant | |
|---|---|---|---|---|---|---|---|
| | | Inlet $SO_2$[1] Monitor | Outlet $SO_2$[1] Monitor | Inlet $NO_x$ Monitor | Outlet $NO_x$ Monitor | Inlet $NO_x$ Monitor | Outlet $NO_x$ Monitor |
| Calibration error | | | | | | | |
| -high level | $\leq 5\%$ | 1.4 | 1.4 | 3.85 | 2.52 | 1.40 | 4.70 |
| -mid level | $\leq 5\%$ | 0.7 | 0.7 | 4.62 | 2.62 | 4.39 | 2.68 |
| Response time | $\leq 15$ min | 0.8 | 1.3 | 1.7 | 0.8 | 1.4 | 1.6 |
| Zero drift (2-hour) | $\leq 2\%$ | 0.25 | 0.25 | 0.64 | 1.04 | 1.20 | 0.05 |
| Calibration drift (2-hour) | $\leq 2\%$ | 0.49 | 0.49 | 1.35 | 1.18 | 1.93 | 1.78 |
| Relative accuracy | $\leq 20\%$[2] | 14.0 | 8.6 | 12.6 | 52.3 | 14.1 | 10.5 |

[1]One instrument was used to measure both inlet and outlet of the reactor.
[2]Alternatively, $\leq 10$ percent of the applicable emissions standard.

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the Method 7 versus the monitor measurements was only 16 ppm on the average.
This is a relatively small difference considering the accuracy of the Method 7.
procedures. At low $NO_x$ levels, similar to those encountered at the reactor
outlet, EPA found the Method 7 analysis to be accurate to only ±35 percent.
A second factor, which indicates that the outlet $NO_x$ monitors performance was
within acceptable limits, is that the performance specifications require the
relative accuracy be less than or equal to 20 percent or 10 percent of the
applicable standard, whichever is greater. Use of the standard as a basis for
relative accuracy calculations is in recognition of the inaccuracy of the
Method 7 analysis at low levels. For example, using the NSPS for bituminous
coal fired sources as a basis, the relative accuracy of the outlet $NO_x$ monitor
is approximately 5 percent, which is within acceptable limits. Because the
relative accuracy of the outlet $NO_x$ monitor was within 10 percent of the
applicable standard and because of the documented poor performance of Method 7
at low $NO_x$ concentrations, it was determined that the outlet $NO_x$ monitor was
performing acceptably.

Overall, the results of the certification tests indicate that the
continuous $NO_x$ and $SO_2$ monitors at both pilot units were performing acceptably.
Therefore, the data collected during the pilot plant tests by Chemico and
UOP are representative of the pilot plant's performance. This is especially
true in light of the extensive monitor maintenance program carried out by
both Chemico and UOP which was designed to insure the accuracy and quality of
the performance data collected.

The preceding discussion presented a summary of the monitor certification
test results. Details of individual measurement results follow. This includes
the results of reference method analysis of calibration gases.

## Calibration Gases

The calibration gases used during the certification tests were analyzed prior to the tests to insure the manufacturer's reported concentrations were accurate. The results of these analyses are presented in Table 3. As shown, the reference method test results were within 5 percent of the manufacturer's reported concentrations except for the mid-range $SO_2$ calibration gas. In this case, the $SO_2$ concentration was assumed to be that determined by the reference method results while the other gas concentrations were assumed equal to the manufacturer's reported concentration.

TABLE 3.  COMPARISON OF MANUFACTURER'S REPORTED CALIBRATION GAS
CONCENTRATIONS WITH REFERENCE METHOD TEST RESULTS

| Calibration Gas | | Reference Method Test Result (ppm) | | | | Error[2] |
| Description | Concentration[1] ppm | 1 | 2 | 3 | Average | (%) |
|---|---|---|---|---|---|---|
| High-Range $SO_2$ | 2690 | 2631 | 2844 | 2792 | 2756 | -2.4 |
| Mid-Range $SO_2$ | 1470 | 1612 | 1618 | 1613 | 1614 | -8.9 |
| Inlet | | | | | | |
| High-Range $NO_x$ | 930 | 914 | 914 | 911 | 913 | +1.9 |
| Mid-Range $NO_x$ | 515 | 464 | 557 | 525 | 515 | 0 |
| Outlet | | | | | | |
| High-Range $NO_x$ | 91.9 | 87.2 | 88.2 | 95.0 | 90.1 | +2.0 |
| Mid-Range $NO_x$ | 50.4 | 54.2 | 51.9 | 43.5 | 49.9 | +1.1 |

[1]This is the manufacturer's reported concentration.
[2]Error = (manufacturer's reported concentration - reference method result)
÷ (reference method result)

## Calibration Error

The calibration error measurements for the HZ pilot plant are presented in Table 4 while the SFGT pilot plant measurements are presented in Table 5. As shown, only one set of data was taken for the $SO_2$ monitor at the SFGT pilot plant since this instrument was used to measure both inlet and outlet concen-

trations. The work-up of the HZ pilot data is presented in Tables 6-9 while the work-up of the SFGT pilot plant data is presented in Tables 10-15. As shown, all the monitors passed the calibration error tests.

TABLE 4. RAW DATA: CALIBRATION ERROR TESTS AT
THE HZ PILOT PLANT

| | Inlet NO$_x$ Monitor[1] | | Outlet NO$_x$ Monitor | |
| Run No. | Calibration Gas Concentration (ppm) | Measurement System Reading (ppm) | Calibration Gas Concentration (ppm) | Measurement System Reading (ppm) |
|---|---|---|---|---|
| 1 | 955 | 948 | 0 | 0.4 |
| 2 | 0 | 2 | 91.9 | 87.2 |
| 3 | 955 | 947 | 50.4 | 49.3 |
| 4 | 515 | 533 | 91.9 | 89.5 |
| 5 | 0 | 4 | 0 | 0.3 |
| 6 | 515 | 532 | 50.4 | 49.2 |
| 7 | 955 | 948 | 0 | 0.3 |
| 8 | 0 | 6 | 91.9 | 89.8 |
| 9 | 955 | 941 | 50.4 | 49.3 |
| 10 | 515 | 538 | 0 | 0.4 |
| 11 | 0 | 5 | 50.4 | 49.3 |
| 12 | 515 | 536 | 91.9 | 89.0 |
| 13 | 0 | 6 | 50.4 | 49.9 |
| 14 | 955 | 955 | 91.9 | 91.0 |
| 15 | 515 | 534 | 0 | 0.4 |

[1]This monitor failed the initial test and was later retested with a different high-range calibration gas.

TABLE 5. RAW DATA: CALIBRATION ERROR TESTS AT THE SFGT PILOT PLANT

| Run No. | Inlet $NO_x$ Monitor | | Outlet $NO_x$ Monitor | | $SO_2$ Monitor | |
|---|---|---|---|---|---|---|
| | Calibration Gas Concentration (ppm) | Measurement System Reading (ppm) | Calibration Gas Concentration (ppm) | Measurement System Reading (ppm) | Calibration Gas Concentration (ppm) | Measurement System Reading (ppm) |
| 1 | 930 | 905 | 0 | 1 | 0 | 0 |
| 2 | 0 | 14 | 515 | 505 | 2690 | 2740 |
| 3 | 930 | 902 | 930 | 916 | 1614 | 1620 |
| 4 | 515 | 495 | 515 | 504 | 2690 | 2688 |
| 5 | 0 | 9 | 930 | 908 | 0 | -4 |
| 6 | 515 | 494 | 0 | 1 | 1614 | 1604 |
| 7 | 930 | 922 | 930 | 907 | 0 | -8 |
| 8 | 0 | 11 | 515 | 501 | 1614 | 1616 |
| 9 | 930 | 922 | 0 | 1 | 2690 | 2664 |
| 10 | 515 | 520 | 515 | 504 | 0 | 0 |
| 11 | 0 | 10 | 0 | 1 | 2690 | 2676 |
| 12 | 515 | 529 | 930 | 916 | 1614 | 1616 |
| 13 | 0 | 5 | 515 | 507 | 2690 | 2680 |
| 14 | 515 | 532 | 930 | 919 | 0 | -4 |
| 15 | 930 | 958 | 0 | 1 | 1614 | 1604 |

TABLE 6.  HZ NO$_x$ INLET MONITOR:  HIGH-RANGE
CALIBRATION ERROR RESULTS

| Run No. | Calibration Gas Concentration (ppm) | Measurement System Reading (ppm) | Difference (ppm) |
|---|---|---|---|
| 1 | 955 | 948 | -7 |
| 3 | 955 | 947 | -8 |
| 7 | 955 | 948 | -7 |
| 9 | 955 | 941 | -14 |
| 14 | 955 | 955 | 0 |
| $\Sigma X_i$ = | | | -36 |
| $|\bar{X}|$ = | | | 7.2 |
| $|CI_{95}|$ = | | | 6.17 |
| Relative Accuracy = | | | 1.4% |

TABLE 7.  HZ NO$_x$ INLET MONITOR:  MID-RANGE
CALIBRATION ERROR RESULTS

| Run No. | Calibration Gas Concentration (ppm) | Measurement System Reading (ppm) | Difference (ppm) |
|---|---|---|---|
| 4 | 515 | 533 | 18 |
| 6 | 515 | 532 | 17 |
| 10 | 515 | 538 | 23 |
| 12 | 515 | 536 | 21 |
| 15 | 515 | 534 | 19 |
| $\Sigma X_i$ = | | | 98 |
| $|\bar{X}|$ = | | | 19.6 |
| $|CI_{95}|$ = | | | 2.99 |
| Relative Accuracy = | | | 4.39% |

TABLE 8. HZ NO$_x$ OUTLET MONITOR: HIGH-RANGE
CALIBRATION ERROR RESULTS

| Run No. | Calibration Gas Concentration (ppm) | Measurement System Reading (ppm) | Difference (ppm) |
|---------|-------------------------------------|----------------------------------|------------------|
| 2       | 91.9                                | 87.2                             | -4.7             |
| 4       | 91.9                                | 89.5                             | -2.4             |
| 8       | 91.9                                | 89.8                             | -2.1             |
| 12      | 91.9                                | 89.0                             | -2.9             |
| 14      | 91.9                                | 91.0                             | -0.9             |
| $\Sigma X_i$ =      |                         |                                  | -13              |
| $|\bar{X}|$ =       |                         |                                  | 2.6              |
| $|CI_{95}|$ =       |                         |                                  | 1.72             |
| Relative Accuracy = |                         |                                  | 4.70%            |

TABLE 9. HZ NO$_x$ OUTLET MONITOR: MID-RANGE
CALIBRATION ERROR RESULTS

| Run No. | Calibration Gas Concentration (ppm) | Measurement System Reading (ppm) | Difference (ppm) |
|---------|-------------------------------------|----------------------------------|------------------|
| 3       | 50.4                                | 49.3                             | -1.1             |
| 6       | 50.4                                | 49.2                             | -1.2             |
| 9       | 50.4                                | 49.3                             | -1.1             |
| 11      | 50.4                                | 49.3                             | -1.1             |
| 13      | 50.4                                | 49.9                             | -0.5             |
| $\Sigma X_i$ =      |                         |                                  | -5               |
| $|\bar{X}|$ =       |                         |                                  | 1                |
| $|CI_{95}|$ =       |                         |                                  | 0.35             |
| Relative Accuracy = |                         |                                  | 2.68%            |

TABLE 10. SFGT $NO_x$ INLET MONITOR: HIGH-RANGE
CALIBRATION ERROR RESULTS

| Run No. | Calibration Gas Concentration (ppm) | Measurement System Reading (ppm) | Difference (ppm) |
|---|---|---|---|
| 1 | 930 | 905 | -25 |
| 3 | 930 | 902 | -28 |
| 7 | 930 | 922 | -8 |
| 9 | 930 | 922 | -8 |
| 15 | 930 | 958 | +28 |
| $\Sigma X_i$ = | | | -41 |
| $|\bar{X}|$ = | | | 8.2 |
| $|CI_{95}|$ = | | | 27.65 |
| Relative Accuracy = | | | 3.85% |

TABLE 11. SFGT $NO_x$ INLET MONITOR: MID-RANGE
CALIBRATION ERROR RESULTS

| Run No. | Calibration Gas Concentration (ppm) | Measurement System Reading (ppm) | Difference (ppm) |
|---|---|---|---|
| 4 | 515 | 495 | -20 |
| 6 | 515 | 494 | -21 |
| 10 | 515 | 520 | 5 |
| 12 | 515 | 529 | 14 |
| 14 | 515 | 532 | 17 |
| $\Sigma X_i$ = | | | -5 |
| $|\bar{X}|$ = | | | 1 |
| $|CI_{95}|$ = | | | 22.77 |
| Relative Accuracy = | | | 4.62% |

TABLE 12.  SFGT NO$_x$ OUTLET MONITOR:  HIGH-RANGE
CALIBRATION ERROR RESULTS

| Run No. | Calibration Gas Concentration (ppm) | Measurement System Reading (ppm) | Difference (ppm) |
|---------|-------------------------------------|----------------------------------|------------------|
| 3 | 930 | 916 | -14 |
| 5 | 930 | 908 | -22 |
| 7 | 930 | 907 | -23 |
| 12 | 930 | 916 | -14 |
| 14 | 930 | 919 | -11 |
| $\Sigma X_i$ = | | | -84 |
| $|\bar{X}|$ = | | | 16.8 |
| $|CI_{95}|$ = | | | 6.65 |
| Relative Accuracy = | | | 2.52% |

TABLE 13.  SFGT NO$_x$ OUTLET MONITOR:  MID-RANGE
CALIBRATION ERROR RESULTS

| Run No. | Calibration Gas Concentration (ppm) | Measurement System Reading (ppm) | Difference (ppm) |
|---------|-------------------------------------|----------------------------------|------------------|
| 2 | 515 | 505 | -10 |
| 4 | 515 | 504 | -11 |
| 8 | 515 | 501 | -14 |
| 10 | 515 | 504 | -11 |
| 13 | 515 | 507 | -8 |
| $\Sigma X_i$ = | | | -54 |
| $|\bar{X}|$ = | | | 10.8 |
| $|CI_{95}|$ = | | | 2.69 |
| Relative Accuracy = | | | 2.62% |

TABLE 14. SFGT SO$_2$ MONITOR HIGH-RANGE
CALIBRATION ERROR RESULTS

| Run No. | Calibration Gas Concentration (ppm) | Measurement System Reading (ppm) | Difference (ppm) |
|---------|-------------------------------------|----------------------------------|------------------|
| 2 | 2690 | 2740 | 50 |
| 4 | 2690 | 2688 | -2 |
| 9 | 2690 | 2664 | -26 |
| 11 | 2690 | 2676 | -14 |
| 13 | 2690 | 2680 | -10 |
| $\Sigma X_i$ = | | | -2 |
| $|\bar{X}|$ = | | | 0.4 |
| $|CI_{95}|$ = | | | 36.59 |
| Relative Accuracy = | | | 1.38% |

TABLE 15. SFGT SO$_2$ MONITOR MID-RANGE
CALIBRATION ERROR RESULTS

| Run No. | Calibration Gas Concentration (ppm) | Measurement System Reading (ppm) | Difference (ppm) |
|---------|-------------------------------------|----------------------------------|------------------|
| 3 | 1614 | 1620 | 6 |
| 6 | 1614 | 1604 | -10 |
| 8 | 1614 | 1616 | 2 |
| 12 | 1614 | 1616 | 2 |
| 15 | 1614 | 1604 | -10 |
| $\Sigma X_i$ = | | | -10 |
| $|\bar{X}|$ = | | | 2 |
| $|CI_{95}|$ = | | | 9.29 |
| Relative Accuracy = | | | 0.70% |

## Response Time

Table 16 presents the results of the response time measurements at the HZ and SFGT pilot plants. As shown all the continuous monitors had response times much lower than the 15 minute limit required by the performance specifications. The relatively rapid response times recorded are due, in part, to the short sample lines (less than 25 meters) at the pilot plants. These results indicate that even though the response time measurements were made in accordance with previous certification procedures (and not the current proposed procedures) the response times of the pilot plant continuous monitors are acceptable.

TABLE 16. RESPONSE TIME DATA FROM THE HZ AND SFGT PILOT PLANTS

| | Response Time (min)[1] | | | | | |
| | HZ Monitors | | SFGT Monitors | | | |
| Test No. | $NO_x$ In | $NO_x$ Out | $NO_x$ In | $NO_x$ Out | $SO_2$ In | $SO_2$ Out |
|---|---|---|---|---|---|---|
| 1 | 1.3 | 1.8 | 1.5 | 0.7 | 0.7 | 1.3 |
| 2 | 1.4 | 1.5 | 3.2 | 0.8 | 0.8 | 1.6 |
| 3 | 1.5 | 1.6 | 0.4 | 0.8 | 0.8 | 1.0 |
| Ave. | 1.4 | 1.6 | 1.7 | 0.8 | 0.8 | 1.3 |

[1]Response time was defined as the time it took the instrument to register 95 percent of a step change in concentration of gas to the monitor.

## Zero and Calibration Drift

As discussed earlier, the pilot plants were operated as experimental units. As a result, the accuracy of the continuous monitors was of critical importance and they were calibrated quite frequently (as often as once an hour). By the strict definition, both the 2- and 24-hour drift tests were not applicable to the pilot plants' continuous monitors. Instead, zero and calibration drift data were collected for the monitors prior to the routine calibration carried out by Chemico and UOP. This gives an indication of the drift experienced by the monitors between routine calibrations and is approximately equivalent to the 2-hour drift tests.

TABLE 17.  HZ PILOT PLANT ZERO AND CALIBRATION
DRIFT TEST RESULTS

| Run No. | Inlet $NO_x$ Monitor[1] | | Outlet $NO_x$ Monitor[2] | |
|---|---|---|---|---|
| | ΔZero (ppm) | ΔCal (ppm) | ΔZero (ppm) | ΔCal (ppm) |
| 1 | -12 | -12 | 0 | 2.7 |
| 2 | 40 | 7 | 0 | -5.0 |
| 3 | 8 | -15 | 0 | -3.0 |
| 4 | -20 | 23 | -0.1 | 2.5 |
| 5 | 0 | 40 | 0 | 3.5 |
| 6 | 7 | -10 | 0.1 | 3.6 |
| 7 | -4 | 13 | 0 | -3.0 |
| 8 | -10 | 10 | 0 | 0 |
| 9 | -35 | 15 | 0 | 4.0 |
| 10 | -1 | 9 | 0 | -4.0 |
| 11 | -3 | 40 | -0.1 | 2.0 |
| 12 | -15 | -30 | -0.1 | -2.0 |
| 13 | -17 | -42 | 0 | 0 |
| 14 | 18 | 39 | 0 | 2.0 |
| 15 | 45 | -25 | -0.1 | -2.0 |
| $X_i$ | 1 | 72 | -0.3 | 1.3 |
| $|\bar{x}|$ | 0.07 | 4.8 | 0.02 | 0.09 |
| $|CI_{95}|$ | 11.91 | 14.45 | 0.03 | 1.69 |
| Error (%) | 1.20 | 1.93 | 0.05 | 1.78 |

[1]The range of this monitor was 0-1000 ppm.

[2]The range of this monitor was 0-100 ppm.

TABLE 18.   SFGT PILOT PLANT ZERO AND CALIBRATION DRIFT TEST RESULTS

| Run No. | Inlet NO$_x$ Monitor | | Outlet NO$_x$ Monitor[1] | | SO$_2$ Monitor | |
|---------|---------------------|---------------------|----------------------|----------------------|----------------------|----------------------|
| | $\Delta$Zero (% of Span) | $\Delta$Cal (% of Span) | $\Delta$Zero (ppm) | $\Delta$Cal (ppm) | $\Delta$Zero (% of Span) | $\Delta$Cal (% of Span) |
| 1 | 1.0 | -0.5 | -0.7 | -4.3 | -0.3 | -0.9 |
| 2 | -0.5 | 0.3 | -4.7 | -2.3 | 0.3 | -0.5 |
| 3 | 0.4 | 1.0 | -4.7 | -3.0 | 0.2 | -0.5 |
| 4 | -0.3 | 1.5 | 1.0 | -2.7 | 0.4 | -0.5 |
| 5 | 0.1 | 1.0 | 0 | -3.0 | 0.3 | -0.3 |
| 6 | -0.5 | -1.3 | 0.7 | -2.3 | 0.2 | -0.3 |
| 7 | -0.2 | -1.8 | -2.0 | 2.0 | 0.3 | -0.4 |
| 8 | -0.1 | -0.1 | -2.0 | 1.3 | 0.4 | -0.4 |
| 9 | -0.5 | -2.0 | -4.3 | 10.0 | 0.2 | -0.7 |
| 10 | -0.5 | -3.5 | 1.0 | 3.7 | -0.2 | 1.0 |
| 11 | -0.5 | 1.1 | 1.3 | 1.7 | -0.4 | 0.3 |
| 12 | -1.0 | 0.4 | 2.0 | -10.0 | 0 | 0.1 |
| 13 | -1.1 | -2.5 | 4.0 | 1.0 | 0.3 | 1.0 |
| 14 | -0.4 | 2.0 | -3.3 | -1.7 | 0 | -0.3 |
| 15 | -1.0 | -2.0 | -4.3 | 3.0 | -0.4 | -0.3 |
| $\Sigma X_i$ | -5.1 | -6.4 | -16 | -6.6 | -1.3 | -2.7 |
| $|\bar{X}|$ | 0.34 | 0.43 | 1.07 | 0.44 | 0.09 | 0.18 |
| $|CI_{95}|$ | 0.30 | 0.92 | 1.54 | 2.51 | 0.16 | 0.31 |
| Error (%) | 0.64 | 1.35 | 1.04 | 1.18 | 0.25 | 0.49 |

[1]The range of this monitor was 0-250 ppm.

## Relative Accuracy

Relative accuracy is the most important of the certification tests conducted since this compares the continuous monitor results to reference method analyses of the flue gas. In addition, the relative accuracy tests provide an independent check of the pilot plants' performance while the other certification tests only yield performance information about the instruments.

Tables 19, 20, and 21 present the raw data and results for the HZ relative accuracy tests while Tables 22 and 23 present this information for the SFGT pilot plant. As shown, all monitors except the $NO_x$ outlet at the SFGT pilot plant meet the performance specifications. The fact that the SFGT outlet $NO_x$ analyzer does not meet the relative accuracy specification is not significant in terms of the performance data collected. The average $NO_x$ reduction recorded by the instruments during the relative accuracy tests was 84.9 percent, while the Method 7 results indicate an average $NO_x$ reduction of 87.4 percent.

TABLE 19. HZ $NO_x$ INLET MONITOR: RELATIVE ACCURACY TEST DATA

| Test No. | Monitor Readings | | Reference Method Results | | |
| | $NO_x$ (ppm wet) | $O_2$ (% wet) | $NO_x$ (ppm dry) | $O_2$ (% wet) | Moisture (%) |
|---|---|---|---|---|---|
| 1 | 485 | 3.4 | 469 | 3.0 | 7.8 |
| 2 | 443 | 3.6 | 442 | 3.0 | 7.0 |
| 3 | 479 | 3.4 | 430 | 2.5 | 8.0 |
| 4 | 469 | 3.3 | 443 | 2.5 | 7.9 |
| 5 | 489 | 3.8 | 439 | 3.0 | 7.5 |
| 6 | 460 | 3.5 | 453 | 3.0 | 8.4 |
| 7 | 435 | 2.8 | 442 | 2.0 | 8.1 |
| 8 | 447 | 2.9 | 469 | 2.5 | 7.9 |
| 9 | 484 | 3.6 | 524 | 3.0 | 8.5 |

TABLE 20. HZ $NO_x$ OUTLET MONITOR: RELATIVE ACCURACY TEST DATA

| Test No. | Monitor Readings | | Reference Method Results | | |
|---|---|---|---|---|---|
| | $NO_x$ (ppm wet) | $O_2$ (% wet) | $NO_x$ (ppm dry) | $O_2$ (% wet) | Moisture (%) |
| 1 | 73.7 | 3.4 | 73.2 | 3.5 | 8.1 |
| 2 | 66.6 | 3.6 | 62.8 | 3.3 | 7.4 |
| 3 | 57.3 | 3.4 | 52.4 | 2.7 | 8.2 |
| 4 | 57.8 | 3.4 | 56.4 | 2.5 | 8.1 |
| 5 | 63.9 | 3.2 | 55.0 | 2.5 | 7.8 |
| 6 | 64.0 | 3.9 | 70.1 | 4.0 | 8.7 |
| 7 | 79.4 | 2.9 | 81.4 | 2.0 | 8.4 |
| 8 | 82.5 | 2.5 | 87.9 | 2.0 | 8.1 |
| 9 | 78.8 | 3.3 | 87.5 | 3.5 | 8.8 |

TABLE 21. HZ NO$_x$ MONITORS: RELATIVE ACCURACY TEST RESULTS

| Test No. | Inlet Monitor | | | Outlet Monitor | | |
| --- | --- | --- | --- | --- | --- | --- |
| | Monitor (lb/10$^6$Btu) | Method 7 (lb/10$^6$Btu) | Difference (lb/10$^6$Btu) | Monitor (lb/10$^6$Btu) | Method 7 (lb/10$^6$Btu) | Difference (lb/10$^6$Btu) |
| 1 | 0.711 | 0.657 | 0.054 | 0.105 | 0.106 | -0.001 |
| 2 | 0.657 | 0.605 | 0.052 | 0.097 | 0.088 | 0.009 |
| 3 | 0.687 | 0.576 | 0.111 | 0.082 | 0.071 | 0.011 |
| 4 | 0.668 | 0.590 | 0.078 | 0.082 | 0.075 | 0.007 |
| 5 | 0.717 | 0.601 | 0.116 | 0.091 | 0.073 | 0.018 |
| 6 | 0.663 | 0.621 | 0.042 | 0.094 | 0.102 | -0.008 |
| 7 | 0.603 | 0.572 | 0.031 | 0.111 | 0.105 | 0.006 |
| 8 | 0.623 | 0.624 | -0.001 | 0.112 | 0.114 | -0.002 |
| 9 | 0.702 | 0.718 | -0.016 | 0.112 | 0.123 | -0.011 |
| $\Sigma X_i$ | - | - | 0.467 | - | - | 0.029 |
| $|\bar{x}|$ | - | 0.618 | 0.052 | - | 0.095 | 0.003 |
| $|CI_{95}|$ | - | - | 0.035 | - | - | 0.007 |
| Relative Accuracy (%) | - | - | 14.1 | - | - | 10.5 |

TABLE 22. SFGT $NO_x$ MONITORS: RELATIVE ACCURACY TEST DATA AND RESULTS[1]

| Test No. | Inlet Monitor | | | Outlet Monitor | | |
|---|---|---|---|---|---|---|
| | Monitor (ppm) | Method 7 (ppm) | Difference (ppm) | Monitor (ppm) | Method 7 (ppm) | Difference (ppm) |
| 1 | 433 | 395 | 38 | 68.7 | 79.4 | -10.7 |
| 2 | 408 | 394 | 14 | 94.7 | 79.2 | 15.5 |
| 3 | 438 | 391 | 47 | 71.9 | 50.6 | 21.3 |
| 4 | 395 | 334 | 61 | 70.0 | 38.6 | 31.4 |
| 5 | 398 | 345 | 53 | 48.0 | 35.1 | 12.9 |
| 6 | 427 | 425 | 2 | 42.3 | 40.7 | 1.6 |
| 7 | 387 | 357 | 30 | 48.3 | 34.8 | 13.5 |
| 8 | 313 | 299 | 14 | 65.0 | 34.5 | 30.5 |
| 9 | 357 | 351 | 6 | 28.3 | 20.6 | 7.7 |
| $\Sigma X_i$ | – | – | 265 | – | – | 123.7 |
| $|\bar{X}|$ | – | 366 | 29.44 | – | 45.9 | 13.7 |
| $|Cl_{95}|$ | – | – | 16.56 | – | – | 10.29 |
| Relative Accuracy (%) | – | – | 12.6 | – | – | 52.3 |

[1] All concentrations are expressed on a wet basis.

TABLE 23.   SFGT $SO_2$ MONITOR:   RELATIVE ACCURACY TEST DATA AND RESULTS[1]

| Test No. | Inlet Monitor | | | Outlet Monitor | | |
| --- | --- | --- | --- | --- | --- | --- |
| | Monitor (ppm) | Method 7 (ppm) | Difference (ppm) | Monitor (ppm) | Method 7 (ppm) | Difference (ppm) |
| 1 | 2412 | 2207 | 205 | 202 | 192 | 10 |
| 2 | 2336 | 2162 | 174 | 198 | 189 | 9 |
| 3 | 2408 | 2145 | 263 | 210 | 205 | 5 |
| 4 | 2440 | 2765 | 175 | 206 | 203 | 3 |
| 5 | 2436 | 2103 | 333 | 144 | 148 | -4 |
| 6 | 2360 | 2120 | 240 | 120 | 119 | 1 |
| 7 | 2460 | 2223 | 237 | 186 | 224 | -38 |
| 8 | 2472 | 2278 | 194 | 182 | 164 | 18 |
| 9 | 2444 | 2048 | 396 | 158 | 141 | 17 |
| $\Sigma X_i$ | - | - | 2217 | - | - | 21 |
| $\lvert \bar{x} \rvert$ | - | 2172 | 246.3 | - | - | 176.1 · 2.3 |
| $\lvert CI_{95} \rvert$ | - | - | 57.7 | - | - | 12.9 |
| Relative Accuracy (%) | - | - | 14.0 | - | - | 8.6 |

[1]All concentrations expressed on a wet basis.

It should be noted that the results of the SFGT relative accuracy tests are expressed as ppm instead of mass emissions of unit heat input to the boiler. This was due to the fact that there was no diluent monitor used at the SFGT pilot plant. While these results do not strictly conform to the performance specifications, they are still valid in terms of establishing process performance. This is due to the fact that the SFGT pilot plant reactor operated under positive pressure and thus no dilution occurred across the reactor. Thus the measured removals represent actual removals and not apparent changes in concentration due to dilution.

APPENDIX D

ECONOMIC PREMISES AND EQUIPMENT
COSTS USED FOR COST ESTIMATE

SECTION 1

INTRODUCTION

This appendix presents the economic premises developed by TVA and used
as a basis for the cost estimate prepared as part of this evaluation. It
also includes the estimated equipment costs which were used to determine the
total capital investment.

# SECTION 2

## ESTIMATED EQUIPMENT COSTS

Table 1 presents the modified estimated equipment costs for the HZ process and compares those costs with the original TVA estimates. For the HZ process, the modified equipment cost estimates were developed based on the ratio of material flowrates or energy requirements and standard exponential factors which relate equipment cost ratios to equipment size ratios. For all equipment except the HZ catalyst, the exponents were taken from the article: "Capital Cost Estimating" by K.M. Guthrie, Chemical Engineering, March 24, 1969. For the HZ catalyst, the costs were determined by assuming that no economy of scale is realized for the catalyst. Costs for the air preheater modifications were based on a previous study completed by Radian entitled "Ammonium Sulfate and Bisulfate Formation in Air Preheaters".

As shown in Table 1, most of the equipment items are projected to decrease slightly in cost. But, the equipment costs based on the pilot plant design includes the cost for air preheater modifications. As a result, there is essentially no change in total equipment costs between the Radian and TVA estimates.

TABLE 1. MODIFIED EQUIPMENT COST ESTIMATES

| Item | Quantity | Description | Total Equipment Cost 1979$ TVA | Radian |
|------|----------|-------------|--------------------------------|--------|
| Area 1 - NH$_3$ Storage and Injection | | | | |
| 1 | 2 | NH$_3$ Unloading Compressor | 50,000 | 46,000 |
| 2 | 8 | NH$_3$ Storage Tanks | 230,000 | 216,000 |
| 3 | 2 | NH$_3$ Vaporizer | 36,800 | 34,400 |
| 4 | 2 | NH$_3$ Air Mixture Blower | 13,500 | 12,600 |
| | Sub-Total Area 1 | | 330,400 | 309,500 |
| Area 2 - Reactor Section | | | | |
| 1 | 2 | Reactor | 1,029,000 | 1,005,200 |
| 2 | | Catalyst | 6,370,000 | 5,125,000 |
| | Sub-Total Area 2 | | 7,399,000 | 6,130,200 |
| Area 3 - Flue Gas Fans | | | | |
| 1 | 4 | Flue Gas Blower | 405,000 | 300,900 |
| | Sub-Total Area 3 | | 405,000 | 300,900 |
| Area 4 - Air Preheater Modifications | | | | |
| 1 | 2 | Modified Air Preheater | - | 1,243,400 |
| | Sub-Total Area 3 | | 0 | 1,243,400 |
| | TOTAL, Areas 1-4 | | 8,134,400 | 8,006,700 |

# SECTION 3

## ECONOMIC PREMISES

This section presents the economic premises developed by TVA and used as a basis for the cost estimates prepared as part of this study.

### Capital Investment

Capital investment estimates were based on a midwestern plant location and represent projects beginning in mid-1977 and ending in mid-1980, with an average cost basis for scaling of mid-1979. Direct investments were calculated using the average annual *Chemical Engineering* cost indices for the period up to 1975 and the recent TVA projections for the period 1976-1981 shown in Table 2. Actual equipment cost estimates are based on 1978 cost information obtained from engineering-contracting, processing, and equipment companies.

Costs related to equipment, material, and construction-labor shortages with accompanying overtime pay incentive and costs for the generation facilities for electricity used by the $NO_x$ removal processes and FGD unit were not included.

TABLE 2. COST INDICES AND PROJECTIONS

| Year | 1970 | 1971 | 1972 | 1973 | 1974 | 1975 | 1976[a] | 1977[a] | 1978[a] | 1979[a] | 1980[a] | 1981[a] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Plant | 125.7 | 132.3 | 137.2 | 144.1 | 165.4 | 182.4 | 197.9 | 214.7 | 232.9 | 251.5 | 271.6 | 293.3 |
| Material[b] | 123.8 | 130.4 | 135.4 | 141.9 | 171.2 | 194.7 | 210.3 | 227.1 | 245.3 | 264.9 | 286.1 | 309.0 |
| Labor[c] | 137.4 | 146.2 | 152.2 | 157.9 | 163.3 | 168.6 | 183.8 | 200.3 | 218.3 | 237.9 | 259.3 | 282.6 |

[a]Projections.

[b]Same as index in *Chemical Engineering* for "equipment, machinery, supports."

[c]Same as index in *Chemical Engineering* for "construction labor."

Direct Investment--

The purchase cost of the process equipment and the cost of materials and labor for the installation of this equipment were included. Also, the cost of piping and insulation, ductwork, excavation, site preparation, foundation, structural, roads and railroads, electrical, instrumentation, buildings, painting, and services required for each unit area were estimated. The costs for the HZ process was estimated based on the flow diagram and equipment lists.

Services, utilities, and miscellaneous costs were estimated at 6% of the total direct investment. This expense covers allocated costs for the use of such power plant facilities as maintenance shops, stores, communications, security, and offices. Parking lots, walkways, landscaping, fencing, and vehicles are also included in the service facility estimate.

Indirect Investment--

The indirect investment includes costs for engineering design and supervision, architect and engineering contractor expenses, construction expenses, contractor fees, and contingency. The engineering design and supervision and contingency factors are based on proven design, not first-of-a-kind installation.

Engineering design and supervision--This indirect investment factor was estimated using a technique that correlates the number of major pieces of process equipment with drafting room man-hour and engineering design costs.

Architect and engineering (A&E) contractor expenses--This cost was based directly upon the engineering design and supervision costs. A&E expense was assumed to be 25% of the portion of engineering design and supervision costs associated with major equipment.

Construction expense--Construction expense was estimated as a function of
the direct investment using the following equation.

$$\text{Construction expense} = 0.25 \ (x)^{0.83}$$

$$\text{where } x = \text{direct investment in \$} \times 10^{-6}$$

Construction facilities (which include costs for mobile equipment, temporary
lighting, construction roads, raw water supply, safety and sanitary facilities,
and other similar expenses incurred during construction) are considered a
part of construction expenses.

Contractor fees--The relationship between contractor fees and total
direct investment used to estimate the cost of contractor fees was:

$$\text{Contractor fees} = 0.096 \ (a)^{0.76}$$

$$\text{where } a = \text{direct investment in \$} \times 10^{-6}$$

Contingency--The contingency was assumed to be 20% of the sum of total
direct investment, engineering design and supervision costs, A&E expenses,
construction expenses, and contractor fees.

Other Capital Charges--

The sum of the total direct and total indirect investment is total
fixed investment. Other capital charges which must be added to this total
fixed investment to obtain the total capital investment are: (1) allowance
for startup and modification, (2) interest during construction, (3) land,
(4) working capital, and (5) royalty fees.

Allowance for startup and modifications--This expense was estimated to
be 10% of the total fixed investment.

Interest during construction--This item was estimated to be 12% of the total fixed investment. This percentage is calculated as the simple interest which would be accumulated at a 10%/yr rate assuming a debt-equity ratio of 60:40 on the incremental capital investment and a 3-year project expenditure schedule as shown in Table 3.

Land--The cost of land was estimated at $3500/acre.

Working capital--Working capital consists of: (1) money invested in raw materials, supplies, and finished products carried in stock and semi-finished products in the process of being manufactured; (2) accounts receivable; (3) cash retained for payment of operating expenses, such as salaries, wages, and raw material purchases; (4) accounts payable; and (5) taxes payable. For these premises, working capital was defined as the equivalent cost of 3 weeks of raw material costs, 7 weeks of direct costs, and 7 weeks of overhead costs. The raw material and direct costs do not include the costs of catalyst replacement.

TABLE 3. PROJECT EXPENDITURE SCHEDULE

| Year | 1 | 2 | 3 | Total |
|---|---|---|---|---|
| Fraction of total expenditure as borrowed funds | 0.15 | 0.30 | 0.15 | 0.60 |
| Simple interest at 10%/yr as % of total expenditure | | | | |
| Year 1 debt | 1.5 | 1.5 | 1.5 | 4.5 |
| Year 2 debt | - | 3.0 | 3.0 | 6.0 |
| Year 3 debt | - | - | 1.5 | 1.5 |
| Accumulated interest as % of total expenditure | 1.5 | 4.5 | 6.0 | 12.0 |

Royalty fees--A royalty fee of $300,000 was assumed for the HZ process. This fee is on the same order as that associated with similar processes.

## Revenue Requirements

Annual revenue requirement calculations are based on 7000 hours of operation per year using mid-1980 operating costs and an average capital charge. Process operation schedules are assumed to be the same as the power plant operating profiles.

## Direct Costs--

Direct operating costs include raw material, labor, utility and maintenance costs. The 1980 projected unit costs for the raw materials were for delivered costs to a midwestern location.

Projected 1980 utility costs are shown in Table 4. Unit costs for electricity and steam generated by the power plant are based on actual production cost including labor, fuel, depreciation, taxes, and rate base return on investment. The electricity rates are based on purchase from an independent source with full capital recovery provided and are adjusted for the quantity used.

Maintenance costs were estimated as a percentage of the direct investment. The maintenance factor depends on operating characteristics of the process and was estimated based on either actual operating experience or maintenance needs in similar process areas. The estimated maintenance factor for the HZ process is 4 percent of indirect investment.

TABLE 4.  PROJECTED 1980 UNIT COST FOR UTILITIES

| Utility | Cost, $ |
|---|---|
| Steam | 2.00/MBtu |
| Electricity | 0.029/kWh |

<u>Indirect Costs--</u>

Indirect costs include capital charges, projected to 1980, and overheads. Following power industry practice, regulated company economics were used for calculating the capital charges. A breakdown of the capital charges is given in Table 5. The depreciation rate is straight line based on the life of the power plant.

TABLE 5. ANNUAL CAPITAL CHARGES FOR POWER INDUSTRY FINANCING

|  | Percentage of total depreciable capital investment |
|---|---|
| Years Remaining Life | 30 |
| Depreciation-straight line (based on years remaining life of power unit) | 3.3 |
| Interim replacements (equipment having less than 30-year life) | 0.7 |
| Insurance and property taxes | 2.0 |
| Total rate applied to original investment | 6.0 |

|  | Percentage of unrecovered capital investment[a] |
|---|---|
| Cost of capital (capital structure assumed to be 60% debt and 40% equity) |  |
| Bonds at 10% interest | 6.0 |
| Equity[b] at 14% return to stockholder | 5.6 |
| Income taxes (Federal and State)[c] | 5.6 |
| Total rate applied to depreciation base | 17.2[d] |

[a] Original investment yet to be recovered or "written off".

[b] Contains retained earnings and dividends.

[c] Since income taxes are approximately 50% of gross return, the amount of taxes is the same as the return on equity.

[d] Applied on an average basis, the total annual percentage of original fixed investment for new (30 year) plants would be 6.0% + 1/2 (17.2%) = 14.6%.

Capital Charges--In estimating the regulated capital charges associated
with FGT, the conventional method of considering the overall life of the power
plant was used. The Federal Power Commission (FPC) recognizes the conclusion of
the National Power Survey that a 30-year service life is reasonable for steam-
electric plants. Because some life spans are less than 30 years, however, FPC
has designated interim replacements as an allowance factor to be used in
estimating annual revenue requirements. Use of this allowance following FPC-
recommended practice provides for financing the cost of replacing such short-
lived units. An average allowance of about 0.35% of the total investment is
normally provided. However, to provide for the unknown life span of $SO_2-NO_x$
control facilities, a larger allowance factor of 0.70% is used for new units.
An insurance allowance of 0.5% is also included in the capital charges based
on FPC practice. Property taxes are estimated at 1.5% of the total depreciable
capital investment.

Debt-equity ratio is another component of capital charges for which
variations of ratios may be expected. FPC data indicate that the long-term
debt for privately owned electric utilities varied only slightly from 51.5
to 54.8% of total capitalization during the period 1965-1973. However, recent
economic trends have changed the incremental debt-equity ratio because
utilities are more dependent on bonds and bank loans for project funding. For
these economic premises the capital structure was assumed to be 60% debt and
40% equity. The interest rate for bonds was assumed to be 10% and the return
to stockholders on equity 14%. Costs of capital and income tax charges were
applied to the uncovered portion of capital investment. Income taxes and
return on equity are each about 50% of gross return. Since return on equity
is 5.6% of total capital investment, income taxes are also 5.6% of total
capital investment. Since most regulatory commissions base the annual permis-
sible return on investment on the remaining depreciation base (that portion
of the original investment yet to be recovered or "written off") a portion
of annual capital charge included in the lifetime operating costs declines
uniformly over the life of the power plant.

Overheads--Plant and administrative overheads vary from company to company. Based on the various methods used in industry and illustrated in a variety of cost estimating sources, the following method of estimating overheads was used. Plant overhead was estimated as 50% of the subtotal conversion costs less utilities, which include the projected costs for labor, maintenance, and analyses. Administrative overhead was estimated as 10% of operating labor and supervision.

Spent Catalyst Disposal--

For the HZ process, the catalyst base support has scrap metal value. Thus, this scrap value yields a credit toward the annual revenue requirement.