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Demonstration of Selective Catalytic Reduction Technology to Control Nitrogen Oxide Emissions From High-Sulfur, Coal-Fired Boilers: A DOE Assessment

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Disclaimer

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Executive Summary

This document serves as the DOE post-project assessment of a project in Round 2 of the Clean Coal Technology (CCT) Program. The Selective Catalytic Reduction (SCR) Demonstration Project was conducted by Southern Company Services (Southern) beginning in June 1990. The operational testing was conducted between July 1993 and July 1995. Southern was a cofunder and Gulf Power Company's Plant Crist served as the host site. Other participants and cofunders were EPRI (formerly the Electric Power Research Institute) and Ontario Hydro. DOE provided 40 percent of the total project cost of $23 million.

SCR technology consists of injecting ammonia (NH_3) into boiler flue gas and passing it through a catalyst bed where nitrogen oxides (NO_X) and NH_3 react to form nitrogen and water vapor.

The objectives of this project were to evaluate:

- Performance of a wide variety of SCR catalyst compositions, geometries, and manufacturing methods at typical U.S. high-sulfur coal-fired utility operating conditions.

- Catalyst resistance to poisoning by trace metal species present in U.S. coals but not present, or present at much lower concentrations, in fuels from other countries.

- Effects on the balance-of-plant equipment from sulfur compounds formed by reactions between sulfur dioxide (SO_2), sulfur trioxide (SO_3), and NH_3 (e.g., plugging and corrosion of downstream equipment).

The catalysts were tested over a 2-year period, during which they were exposed to flue gas from a coal-fired boiler at Plant Crist under commercial installation conditions. Six catalyst suppliers (two U.S., two European, and two Japanese) provided eight different catalysts.

The SCR demonstration project successfully met all objectives. All eight catalysts met design specifications, providing at least 80 percent NO_X removal at an NH_3 slip of 5 ppm or less. Although the catalysts varied somewhat in operating characteristics, such as activity and pressure drop, no one catalyst was found to be superior. Both plate and honeycomb catalysts performed satisfactorily. Catalyst deactivation proceeded as expected, based on European and Japanese experience. Although the Plant Crist test results indicate that no catastrophic deactivation would be expected, catalyst replacement frequency for high-sulfur U.S. coals remains uncertain.

The oxidation rate of SO_2 to SO_3 varied significantly among the catalysts tested. The amounts of ammonium sulfate and ammonium bisulfate formed were sufficient to require periodic washing of the air preheaters, and there was evidence for deposition of these salts on the catalysts. Overall, the pressure drop across the catalyst beds over time was stable, indicating that the soot-blowing procedures used in the test program were satisfactory. Performance comparisons

between high-dust and low-dust reactor configurations were inconclusive because of problems associated with the design of the low-dust reactor.

Southern also performed an economic study of implementing SCR technology. The base-case economics were estimated for an SCR unit installed in a new power plant, using a projected process design that incorporates improvements based on experience gained from the SCR demonstration project. The boiler is assumed to be either a wall-fired or a tangentially fired unit, equipped with low-NO_X burners, and burning 2.5 wt% sulfur coal. Design NO_X concentration at the reactor inlet is 0.35 lb/10^6 Btu. NO_X reduction is assumed to be 60 percent, giving an outlet concentration of 0.14 lb/10^6 Btu, with a design NH_3 slip of 5 ppm.

Based on these assumptions, the capital cost ranges from $45/kW at a capacity of 700 MWe to $61/kW at 125 MWe. Levelized cost on a current dollar basis range from $2,165/ton of NO_X removed for a 700 MWe plant to $2,811/ton at 125 MWe.

Six commercial SCR units have been installed and are operating on low- and medium-sulfur U.S. coals. Because SCR is applicable to almost any kind of boiler, many utilities will likely consider SCR technology in their compliance planning efforts, especially in light of increasingly stringent limitations on NO_X emissions.

I   Introduction

The goal of the U.S. Department of Energy (DOE) Clean Coal Technology (CCT) program is to furnish the energy marketplace with a number of advanced, more efficient, and environmentally responsible coal utilization technologies through demonstration projects. These projects seek to establish the commercial feasibility of the most promising advanced coal technologies that have developed beyond the proof-of-concept stage.

This document serves as a DOE post-project assessment of a project selected in CCT Round 2. The project is described in the report *Demonstration of Selective Catalytic Reduction (SCR) Technology for the Control of Nitrogen Oxide (NO$_X$) Emissions from High-Sulfur, Coal-Fired Boilers* (Southern Company Services 1990).

In June 1990, Southern Company Services (Southern) entered into a cooperative agreement to conduct the study. Southern was a cofunder and served as the host at Gulf Power Company's Plant Crist. Other participants and cofunders were EPRI (formerly the Electric Power Research Institute) and Ontario Hydro. DOE provided 40 percent of the total project cost of $23 million.

The long-term operation phase of the demonstration was started in July 1993 and was completed in July 1995. This independent evaluation is based primarily on information from Southern's Final Report (Southern Company Services 1996).

The SCR process consists of injecting ammonia (NH$_3$) into boiler flue gas and passing the flue gas through a catalyst bed where the NO$_X$ and NH$_3$ react to form nitrogen and water vapor.

The objectives of the demonstration project were to investigate:

- Performance of a wide variety of SCR catalyst compositions, geometries, and manufacturing methods at typical U.S. high-sulfur coal-fired utility operating conditions.

- Catalyst resistance to poisoning by trace metal species present in U.S. coals but not present, or present at much lower concentrations, in fuels from other countries.

- Effects on the balance-of-plant equipment from sulfur compounds formed by reactions between sulfur dioxide (SO$_2$), sulfur trioxide (SO$_3$), and NH$_3$ (e.g., plugging and corrosion of downstream equipment).

The Clean Air Act, initially promulgated in 1970, established New Source Performance Standards (NSPS) for emissions of SO$_2$, NO$_X$, and particulates, among other pollutants, from stationary coal-fired power plants. These regulations were made more stringent in the Clean Air Act Amendments (CAAA) of 1990. The SCR process is one way to meet the NO$_X$ emissions requirements of the CAAA.

II   Technical and Environmental Assessment

II.1 Promise of the Technology

This project was undertaken to evaluate the performance and economics of the SCR process for removing NO_X from the flue gas of boilers fired with U.S. high-sulfur coals. A major advantage of SCR is that the reaction products, nitrogen and water, are innocuous compounds already present in air. The SCR process was initially developed in the United States. The process is widely used in Japan and Europe, including numerous installations on coal-burning power plants. Technical uncertainties associated with applying SCR to plants burning U.S. high-sulfur coals primarily involved the danger of forming excessive amounts of ammonia-sulfur compounds with the attendant plugging and corrosion of downstream equipment. There was also concern over the presence of trace metals such as arsenic, since they can lead to catalyst deactivation.

The SCR demonstration project at Plant Crist was designed to evaluate the performance and cost of SCR technology under typical boiler conditions in the United States. If successful, the process could provide a means of meeting increasingly more stringent NO_X emission regulations for U.S. coal-burning power plants.

The Clean Air Act was originally passed in 1967. It was amended in 1970, 1977, and most recently in 1990. The CAAA of 1990 authorized the U.S. Environmental Protection Agency (EPA) to establish emissions standards for a number of atmospheric pollutants, revising and expanding standards for emissions of SO_2 and NO_X. The CAAA mandates updating of the emissions standards every 5 years.

NO_x Emissions Regulations

Two major portions of the CAAA relevant to NO_X control are Title I and Title IV. Title I establishes National Ambient Air Quality Standards (NAAQS) for six criteria pollutants, including ozone. Title IV addresses controls for specific types of boilers, including coal-fired units. Title IV is often referred to as the Acid Rain Program.

Title IV uses a two-phase NO_X control strategy. Phase I, which had an implementation deadline of January 1, 1996, established regulations for 256 Group 1 boilers: dry-bottom, wall-fired boilers, and tangentially fired (T-fired) boilers. In Phase II, which requires compliance by January 1, 2000, lower emission limits are set for Group 1 boilers, and limits are set for 145 Group 2 boilers, which include cell-burners, cyclones, wet-bottom, wall-fired boilers, and other types of coal-fired boilers. In addition, another 607 wall-fired and T-fired boilers must meet the applicable Phase II limits. The final emission limits under Title IV, promulgated in February 1998, are shown in Table 1.

Table 1. Title IV NO$_X$ Emissions Limits
(lb/10^6 Btu)

Implementation Deadline	Phase I, January 1, 1996	Phase II, January 2, 2000
Group 1 Boilers Dry Bottom Wall-Fired	0.50	0.46
Tangentially Fired	0.45	0.40
Group 2 Boilers Wet Bottom Wall-Fired > 65 MWe	NA	0.84
Cyclone-Fired > 155 MWe	NA	0.86
Vertically Fired	NA	0.80
Cell Burner	NA	0.68
Fluidized Bed	NA	Exempt
Stoker	NA	Exempt

NA = Not applicable

When NO$_X$ and volatile organic compounds (VOCs) enter the atmosphere, they react in the presence of sunlight to form ground-level ozone, which is the major ingredient of smog. The federal Title I NO$_X$ requirements are as follows:

•   Existing major stationary sources must apply reasonably available control technologies (RACT)

•   New or modified major stationary sources must offset their new emissions and install controls representing the best available control technology (BACT)

•   Each state must include ozone control in its State Implementation Plan (SIP).

The current NAAQS for ozone is 0.12 ppm (1-hour average). At this level, many large- and medium-size urban areas are classified as nonattainment and many power plants are within these nonattainment areas. Furthermore, the Northeast Ozone Transport Region (NOTR) is a 13-state area that is considered nonattainment with respect to ozone.

EPA proposed more stringent NAAQS for ozone: 0.08 ppm (8-hour average). An area would be considered nonattainment when the third highest daily maximum 8-hour concentration, averaged over 3 years, is above 0.08 ppm. EPA is also seeking comment on a standard of 0.07 ppm.

The primary technology currently used in utility boilers for NO$_X$ reduction is low NO$_X$

burners (LNBs), which have generally proven adequate to meet Title IV emissions requirements. Field experience with LNBs in the CCT Program provided the data required to establish the current regulations. However, the lower NO_X target levels being considered under Title I may force utilities subject to the most stringent requirements to install LNBs combined with SCR, or alternatively, SCR alone.

History of the SCR Process

Selective catalytic reduction of NO_X using NH_3 as the reducing gas was patented in the U.S. by Englehard Corporation in 1957. The original catalysts, employing platinum or platinum group metals, were unsatisfactory because of the need to operate in a temperature range in which explosive ammonium nitrate forms. Other base metal catalysts were found to have low activity. Research done in Japan in response to severe environmental regulations in that country led to the development of vanadium/titanium catalysts, which have proved successful. This combination forms the basis of current SCR catalyst technology.

In addition to Japan, several countries in Western Europe have enacted stringent NO_X emission regulations that essentially mandate the installation of SCR, and extensive catalyst development work has been done, especially in Germany. As a result, SCR has been used on numerous boilers in Europe. Furthermore, encouraged in part by the initial success of the SCR test program at Plant Crist, there are now six commercial installations of SCR on coal-burning power plants in the U.S. Worldwide installations of SCR on coal-fired utility boilers are summarized in Table 2.

**Table 2. Worldwide Installations of SCR on
Coal-Fired Utility Boilers, 1996 Data**

Country/Region	Capacity, MWe
Austria	1,200
Germany	33,000
Japan	7,700
Netherlands	1,000
Scandinavia	1,100
United States	2,000
Total	46,000

II.2 Process Description

Figure 1 is a schematic that illustrates SCR process.
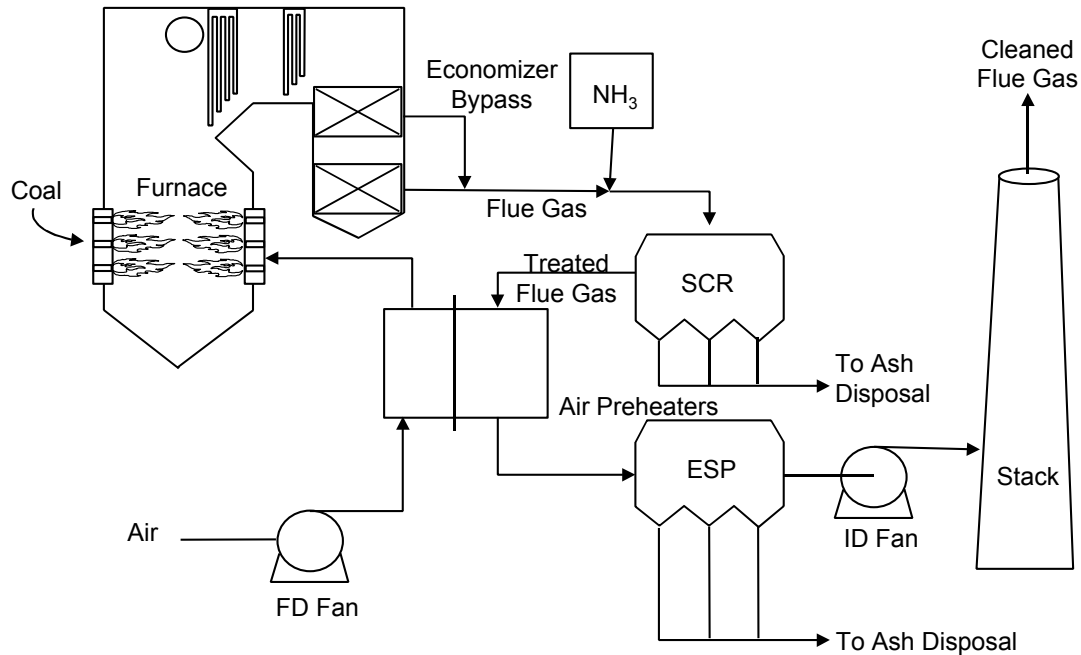
Figure 1. Block Flow Diagram of SCR Installation

NO_X, which consists primarily of NO and NO_2, is converted to nitrogen by reacting with ammonia (NH_3) in the presence of oxygen, according to the following equations:

$$4NO + 4NH_3 + O_2 \Rightarrow 4N_2 + 6H_2O \tag{1}$$
$$2NO_2 + 4NH_3 + O_2 \Rightarrow 3N_2 + 6H_2O \tag{2}$$

Since the NO_X contained in flue gas derived from coal-fired boilers is primarily NO, the first reaction predominates. Sulfur present in the coal is oxidized to SO_2 in the boiler. A small percentage of the SO_2 is also oxidized to SO_3 in the boiler according to the following equation:

$$SO_2 + \frac{1}{2}O_2 \Rightarrow SO_3 \tag{3}$$
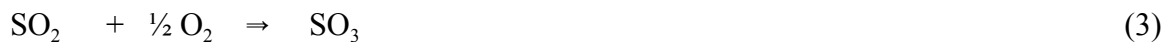
Thus, SO_3 levels at the boiler exit will typically increase as sulfur content of the coal increases. In addition, a portion of the SO_2 is oxidized over the SCR catalyst by the same equation.

The following side reactions produce undesirable by-products: ammonium sulfate, $(NH_4)_2SO_4$, and ammonium bisulfate, NH_4HSO_4.

$$2NH_3 + SO_3 + H_2O \;\Rightarrow\; (NH_4)_2SO_4 \hspace{6cm} (4)$$
$$NH_3 + SO_3 + H_2O \;\Rightarrow\; NH_4HSO_4 \hspace{6cm} (5)$$

Because of these side reactions, it is essential to minimize the amount of unreacted NH_3 in the flue gas downstream of the SCR reactor. This quantity is referred to as NH_3 slip and, in general, must be held below 5 ppm and preferably 2 to 3 ppm. As indicated, the NH_3 slip reacts with small quantities of SO_3 in the SCR reactor exit to form $(NH_4)_2SO_4$ and NH_4HSO_4, which can plug and corrode downstream equipment. This is a greater problem with high-sulfur coals, because of the higher SO_3 levels that result from greater quantities of fuel-generated SO_3 in the boiler and further oxidation of SO_2 in the SCR reactor.

Since SCR catalysts are relatively expensive, it is essential to maximize space velocity and thus minimize catalyst volume for a given application. At the same time, the rate of oxidation of SO_2 to SO_3 must be minimized, which is more temperature sensitive than the SCR reaction. The optimum operating temperature for the SCR process using titanium and vanadium oxide catalysts is about 650 to 750 °F. Some installations use an economizer bypass to maintain the desired flue gas temperature in the reactors during low load operation.

SCR systems can be installed at any of three locations in a power plant:

- Upstream of the air preheater (APH) and electrostatic precipitator (ESP), referred to as hot-side, high-dust.

- Upstream of the APH and downstream of the ESP, hot-side, low-dust.

- Downstream of the APH and ESP, cold-side, low-dust.

In the Plant Crist tests, which operated on a slipstream from the power plant flue gas, each reactor was located upstream of the APH; thus, these were hot-side installations. Seven of the eight reactors were also high-dust installations. The Plant Crist installation is shown in Figure 2.

In commercial practice, most SCR reactors are hot-side, high-dust installations. This location is preferred because it obviates the need to reheat the flue gas to reaction temperature, thereby minimizing loss of thermal efficiency.

SCR catalysts are generally made of a ceramic material that is a mixture of substrate (titanium oxide) and active components (oxides of vanadium and, in some cases, tungsten). The two leading shapes of SCR catalyst used today are honeycomb and plate. Both types were tested at Plant Crist. The honeycomb form usually is an extruded ceramic with the catalyst either incorporated throughout the structure (homogeneous) or coated on the substrate. In plate geometry, the support material is generally coated with a catalyst. When processing flue gas that contains dust, the reactors are typically vertical, with a down flow of flue gas. The catalyst is typically arranged in a series of two to four beds or layers. For systems operating at about 80-percent NO_X reduction, it is common to use three or four layers, and to include provisions for an additional layer, which is not initially installed. This arrangement permits optimization of the catalyst
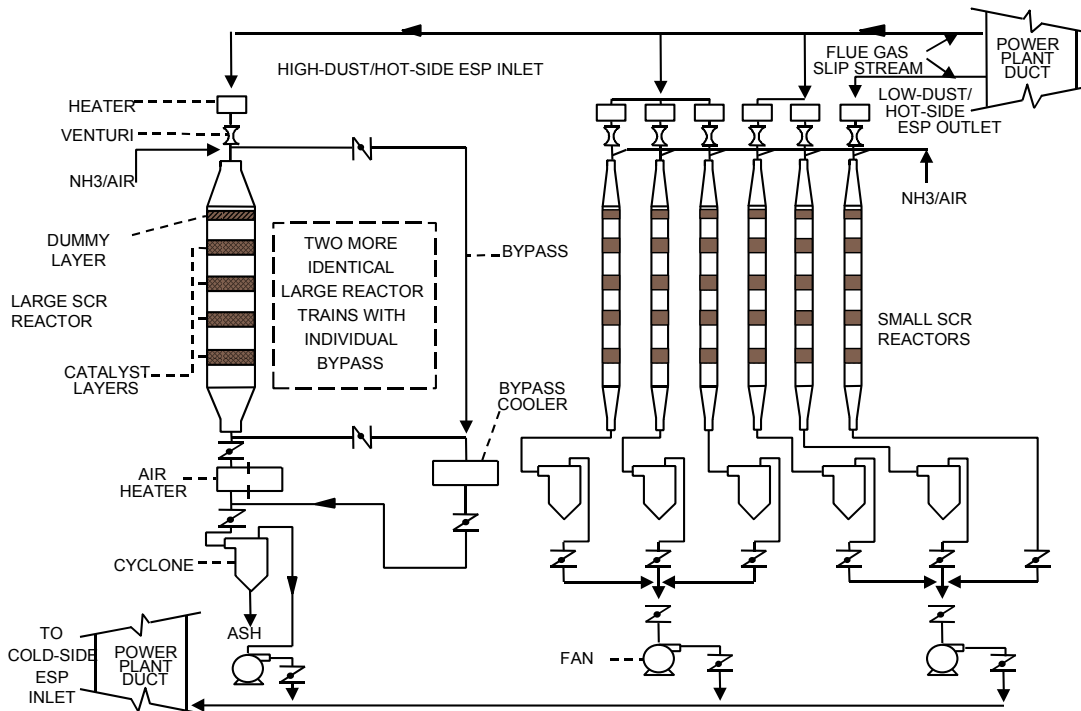
Figure 2. Prototype SCR Demonstration Facility, Process Flow Diagram

management plan to allow for catalyst deactivation, additional NO_X reduction requirements, or both in a more cost effective manner.

As the catalyst activity declines, additional catalyst is installed in the available spaces in the reactor. As deactivation continues, the catalyst is replaced on a rotating basis, one layer at a time, starting with the top. This strategy results in maximum catalyst utilization. The catalyst is subjected to periodic soot-blowing to remove deposits, using steam as the cleaning agent.

II.3 Project Objectives and Results

The goal of this project was to evaluate SCR technology for reducing NO_X emissions from utility boilers burning U.S. coals. The project was designed to confirm pilot-plant results and to develop scaleup procedures necessary for commercial application of the technology, as well as to resolve those technical issues that could not be adequately addressed in an engineering study.

The objectives of this project were to investigate:

• Performance of a wide variety of SCR catalyst compositions, geometries, and manufacturing methods at typical U.S. high-sulfur coal-fired utility operating conditions.

• Catalyst resistance to poisoning by trace metal species present in high-sulfur U.S. coals

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but not present, or present at much lower concentrations, in fuels from other countries.

- Effects on the balance-of-plant equipment from sulfur compounds formed by reactions between SO_2, SO_3, and NH_3 (e.g., plugging and corrosion of downstream equipment)

Six catalyst suppliers (two U.S., two European, and two Japanese) provided eight catalysts with various chemical compositions and shapes (plate or honeycomb). Catalyst suppliers were given latitude in designing their catalyst offerings to meet a minimum of 80-percent NO_X reduction for long-term baseline conditions. All catalysts performed well, yielding NO_X removal rates of 80 percent or better with acceptable NH_3 slip.

Higher rates of NO_X removal, up to 90 percent or more, may be achievable for some units, depending on plant characteristics, but for most commercial applications, the NO_X removal rate will likely be limited to about 80 percent. Careful system design and process control are required to avoid excessive NH_3 slip, especially at the higher conversion levels.

II.4 Environmental Performance

The environmental impact of the SCR demonstration project is covered in a separate report (Radian Corporation 1996). The project had only a minor effect on air quality at Plant Crist, because only a relatively small flue gas slipstream was treated. Likewise, there was no detectable impact on water quality in the ash pond discharge stream. However, the environmental impacts of the technology studied in the test program are significant. SCR has been shown to provide high levels of NO_X removal with minimal NH_3 slip.

II.5 Post-Demonstration Achievements

SCR units are being operated in six commercial coal-fired power plants in the United States, on coals ranging in sulfur content from about 0.8 to 2.0 wt%. Data from the demonstration project and the subsequent commercial applications have shown that SCR can routinely achieve the required levels of NO_X reduction to comply with present and anticipated environmental regulations.

III   Operating Capabilities Demonstrated

III.1   Size of Unit Demonstrated

The demonstration project was conducted at Gulf Power's Plant Crist, located near Pensacola, Florida. Plant Crist consists of seven fossil fueled generating units. Units 1, 2, and 3 are small gas- and oil-fired boilers, and Units 4 through 7 are coal-fired. The SCR test facility was built in and around the duct work on Unit 5. This unit is a tangentially fired, dry-bottom boiler, rated at 75 MWe (gross), built by Combustion Engineering and placed into operation in 1961. The unit is equipped with hot-side and cold-side ESPs for particulate control.

As shown in Figure 2, the individual SCR reactors operated on a slipstream taken from the flue gas of Unit 5. There were three 2.5-MWe equivalent reactors and six 0.20-MWe equivalent reactors, each containing a different catalyst for side-to-side performance comparisons. Eight of the nine reactors were designed to treat the flue gas containing full particulate loading (high-dust), extracted from the inlet duct of the hot-side ESP. One small reactor was designed to treat flue gas extracted from the hot-side ESP outlet (low-dust). Because of a reactor design problem, it was not possible to fully evaluate the differences in performance between the single low-dust reactor and the high-dust units.

Each reactor train was equipped with an electric duct heater to independently control flue gas temperature and a venturi meter to measure the flue-gas flow rate. An economizer bypass line maintained a minimum flue gas temperature of 620 °F to the high dust reactors. Anhydrous NH_3 was independently metered to a stream of heated dilution air and was injected by nozzles into the flue gas upstream of each SCR reactor. The flue gas containing NH_3 passed through the reactors, each of which had the capacity to contain up to four catalyst layers.

For each of the larger reactor trains, the flue gas exiting the reactor entered a specially modified pilot-scale APH, each of different design. The modified APHs were used to better simulate full-scale APHs and thus improve the extrapolation of results to commercial scale. The APHs were incorporated in the project to evaluate the effects of the SCR on APH deposit formation and the effects of the deposits on APH performance and operation.

All reactor trains except the low-dust train had a cyclone downstream of the SCR reactor to protect the induced draft fans from particulates. The exhausts from all of the SCR reactors were combined into a single manifold and reinjected into the host boiler's flue gas stream ahead of the cold-side ESP. The preheated air streams from the APH on the larger reactors were also combined into a single manifold and returned to the host boiler draft system at the existing host APH outlet. All particulate matter removed from the test facility was combined with ash from the host unit's ESP and sent to ash disposal.

The test facility examined the performance of eight SCR catalysts (one reactor was idled because of the withdrawal of a project participant), differing in chemical makeup and physical

form. Each catalyst supplier was given great latitude in designing the catalyst offering, provided it met the following requirements:

- Catalyst baskets that match predetermined reactor dimensions.
- A maximum of four catalyst layers.
- A maximum baseline SO_2 oxidation rate of 0.75 percent.
- A maximum baseline slip of 5 ppm.
- A minimum 80-percent NO_X reduction at baseline conditions.
- A 2-year life while meeting the above performance criteria.

Full-scale demonstration of SCR technology was not required, since the major issues to be addressed were questions of chemistry, which could be adequately investigated using a slipstream facility. A full-scale facility would have been unnecessarily expensive while providing little additional technical information. However, the catalyst modules used in the reactors were full-scale versions of the catalysts used commercially in Europe and Japan. The test units were designed to ensure that the flue gas slipstreams were fully representative in terms of gaseous and solid species and that the catalyst modules were exposed to flue gas conditions identical to those experienced in full-scale installations. In general, the performance of fixed-bed catalytic reactors can readily be scaled up.

The tests were conducted on flue gas derived primarily from burning Illinois No. 6 coal, a typical midwestern high-sulfur (2.3 percent sulfur) coal widely used for power generation. Coal properties are given in Table 3.

Table 3. Properties of Coal Used in Plant Crist Tests
(Coal source: Illinois No. 6 Bituminous)

Proximate Analysis, wt% (as received)

Fixed Carbon	47.65
Volatile Matter	34.16
Moisture	9.80
Ash	8.39
Total	**100.00**
HHV, Btu/lb	100.00

HHV = higher heating value

Ultimate Analysis, wt% (as received)

Carbon	67.48
Hydrogen	4.51
Nitrogen	1.43
Sulfur	2.33
Chlorine	0.14
Oxygen	5.92
Ash	8.39
Water	9.80
Total	**100.00**

III.2 Performance Level Demonstrated

Over the 2-year test period, operating experience with individual catalysts ranged from 4,000 to 13,000 hours. Parametric testing was conducted every 4 to 6 months. Catalysts were provided initially by three U.S. suppliers (Englehard, Grace, and Cormetech), two European suppliers (Haldor Topsoe and Siemens), and two Japanese suppliers (Hitachi Zosen and Nippon Shokubai). Englehard subsequently withdrew from the project, and its low-dust catalyst was replaced by one of Cormetech's available low-dust catalysts. The catalysts tested in this project are listed in Table 4.

Table 4. SCR Catalysts Tested at Plant Crist

Reactor	Catalyst Supplier	Reactor Size	Dust Level	Composition	Catalyst Configuration
A	W.R. Grace (Noxeram)	Large	High	V-W/Ti	Honeycomb
B	Nippon Shokubai K.K.	Large	High	V-W/Ti-Si	Honeycomb
C	Siemens AG	Large	High	V/Ti	Plate
D	W.R. Grace (Synox)	Small	High	V/Ti-Si	Honeycomb
E	Cormetech	Small	High	V-W/Ti	Honeycomb
F	Haldor Topsoe	Small	High	V/Ti	Plate
G	Hitachi Zosen	Small	High	V/Ti	Plate
J	Cormetech	Small	Low	V-W/Ti	Honeycomb

All of the catalysts performed well in both parametric and long-term testing, achieving at least 80-percent NO_X removal with a maximum NH_3 slip of 5 ppm. Although the catalysts varied somewhat in operating characteristics, such as activity and pressure drop, no one catalyst was found to be superior. Catalyst deactivation proceeded as expected, based on European and Japanese experience. Extrapolating the test data to 16,000 hours suggests an average decrease in activity of about 20 percent, although in practice this decrease could range from 10 to 30 percent.

Although no catastrophic deactivation effects could be attributed to the use of high-sulfur U.S. coals, catalyst replacement frequency remains uncertain. No detrimental effects of trace metals such as arsenic were detected. However, the accumulation of trace metals on the surface of the catalysts was clearly evident in the laboratory tests.

Both plate and honeycomb catalysts performed satisfactorily. A major difference between these catalyst configurations is pressure drop, which must be taken into account in designing commercial SCR installations.

The overall stability of the pressure drop across the catalyst beds over time indicated that the soot-blowing procedures used in the test program were satisfactory. Performance comparisons between high-dust and low-dust reactor configurations were inconclusive because of problems associated with the design of the low-dust reactor. There was significant variation in the rate of oxidation of SO_2 to SO_3 among the catalysts tested. The amounts of $(NH_4)_2SO_4$ and NH_4HSO_4 formed were sufficient to result in corrosion and plugging of the APHs downstream of the SCR reactors, requiring periodic washing and indicating the need to choose appropriate materials of construction for APHs for commercial SCR installations.

III.3   Major Operating and Design Variables Studied

Testing consisted of long-term studies of catalyst deactivation as well as parametric tests to investigate the effects of operating variables. The purpose of the parametric tests was to study the effects of several variables, including reactor operating temperature, NH_3/NO_X molar ratio, and space velocity.

Long-Term Testing of Catalyst Deactivation

The results of the long-term catalyst tests are expressed in terms of the decrease in activity over time. The rate constant, k, is defined in the following kinetic equations from S.M. Cho of Foster Wheeler (Cho 1994):

$$k/SV = -\ln(1-x/r), \text{ and} \tag{6}$$
$$s = (r-x)N_o \text{ or } r = x + s/N_o, \tag{7}$$

where k = rate constant; SV = space velocity; x = fractional conversion of NO_X; r = molar ratio of NH_3 to NO_X at reactor inlet; s = NH_3 slip; and N_o = NO_X concentration at the reactor inlet.

These equations assume that the SCR reaction is first order with respect to NO_X or NH_3. Work by Rao, McIlvried, and Mann (1994) and Baldwin, Smith and others (1995) has shown that the process can be better represented by a modified Langmuir-Hinshelwood relationship, as follows:

$$k/SV = -\ln(1-x/r) + \ln[(1-x)/(1-x/r)]/KN_o(1-r), \tag{8}$$

where K = adsorption coefficient of NO_X on the catalyst.

The latter kinetic relationship more accurately predicts the space velocity (and hence catalyst volume) required to both remove NO_X and minimize NH_3 slip, especially at higher conversion levels.

From a practical standpoint, the precise kinetic relationship is of little concern. What is important is the ratio k/k_o, where k is the rate constant at a given time in the deactivation cycle and k_o is the initial rate constant with fresh catalyst. This ratio, and thus catalytic activity, is determined by dividing the fractional NO_X conversion at a given time by the conversion at time zero. The results for the SCR test program at Plant Crist are summarized in Figure 3, which shows the k/k_o ratio as a function of time. The relative activity begins at 1.0 at time zero and decreases to an average of about 0.8 at 12,000 hours (about 1.5 years).
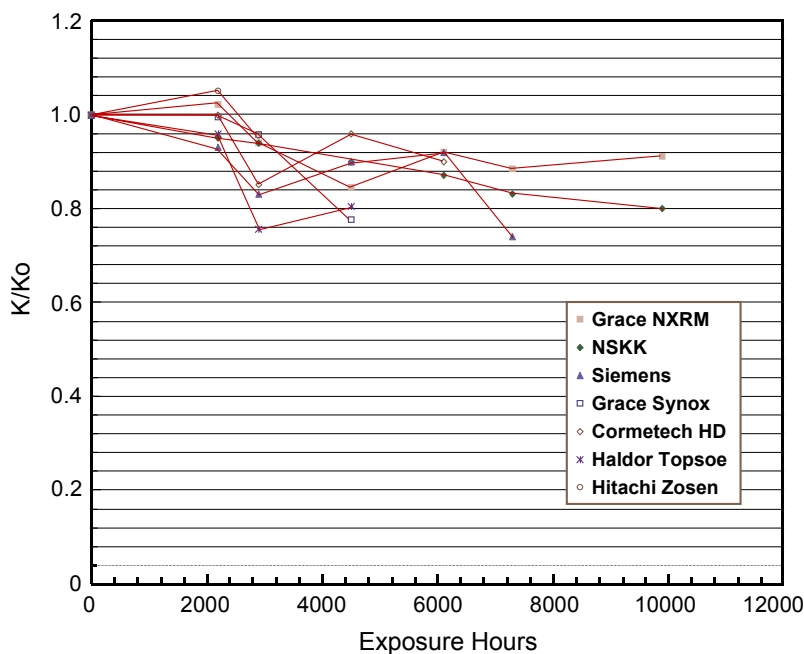

Figure 3. K/K$_o$ Versus Exposure Time

Parametric Studies

The parametric studies investigated the effects of reactor operating temperature, NH_3/NO_X molar ratio, and space velocity on catalyst performance. Five sets of parametric data were obtained. The results are summarized in the following paragraphs. Some of the data refer to a single parametric study and are not necessarily representative of overall performance.

- **Effect of Temperature on Ammonia Slip:** The parametric tests covered the range of 620 to 750 °F, with a design operating temperature of 700 °F. Figure 4 shows that as temperature was increased while maintaining a constant 0.8 NH_3/NO_X ratio, NH_3 slip remained fairly constant at less than 5 ppm for most of the catalysts. The exception was the Grace SNX catalyst — the NH_3 slip was 10 ppm at the lowest temperature, decreasing to the same level as the other catalysts at the higher temperatures.

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Figure 4. Ammonia Slip Versus Flow Rate
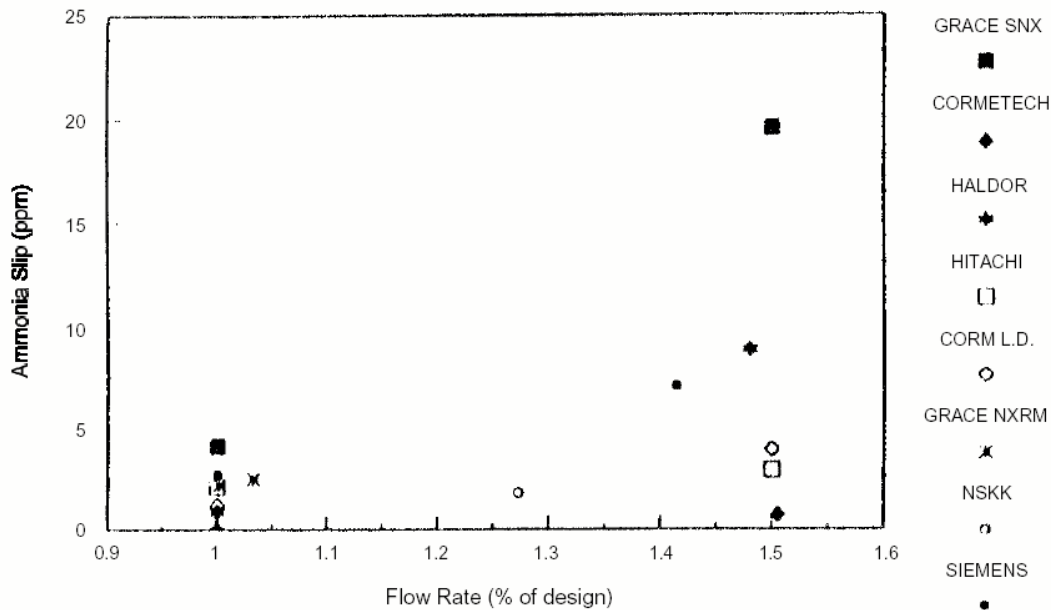
.8 NH$_3$/NO$_x$ ratio, standard flow
Third parametric data set

- **Effect of NH$_3$/NO$_x$ Ratio:** The parametric tests covered a ratio range of 0.6 to 1.0, with a design NH$_3$/NO$_X$ molar ratio of 0.8. The results are shown in Figure 5. Except for one catalyst, NH$_3$ slip remained constant at about 2 ppm at low levels of the NH$_3$/NO$_X$ ratio, increasing dramatically above a ratio of about 0.9.

- **Effect of Space Velocity:** The effect of space velocity on NH$_3$ slip is shown in Figure 6. At an operating temperature of 700 °F and an NH$_3$/NO$_X$ ratio of 0.8, increasing the gas flow rate (and hence the space velocity) from 100 to 150 percent of the design value resulted in a fairly constant NH$_3$ slip of less than 5 ppm for three of the catalysts. NH$_3$ slip increased to significantly greater than 5 ppm for the other three catalysts studied in this part of the test program.

- **Effect of Temperature on SO$_2$ Oxidation:** Figure 7 shows that as the temperature was increased, the rate of SO$_2$ oxidation was fairly constant at less than 0.2 percent for two of the catalysts, while increasing to varying degrees for the other catalysts.
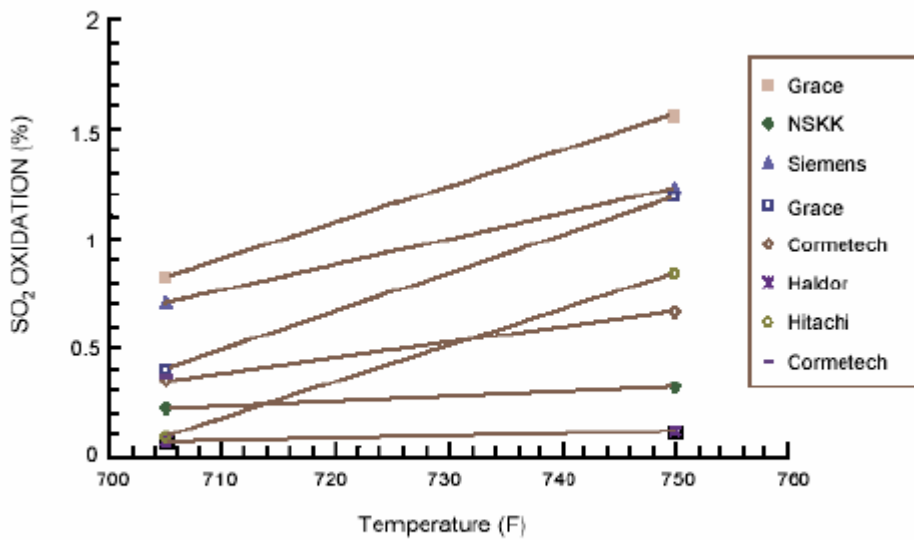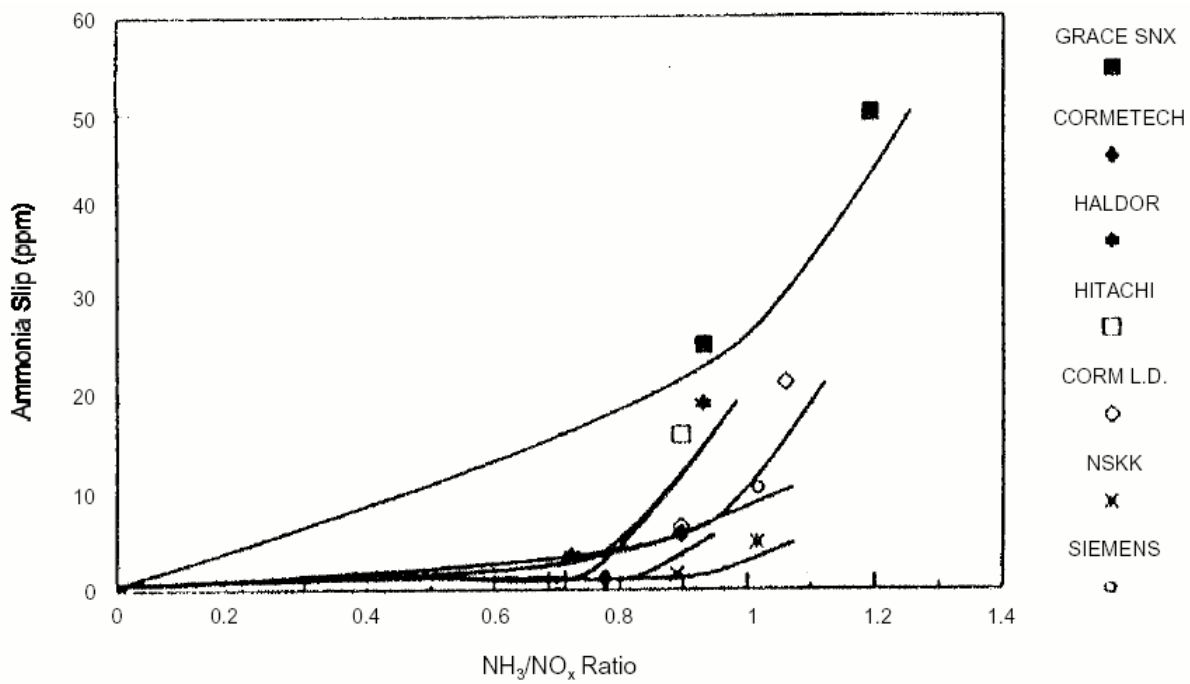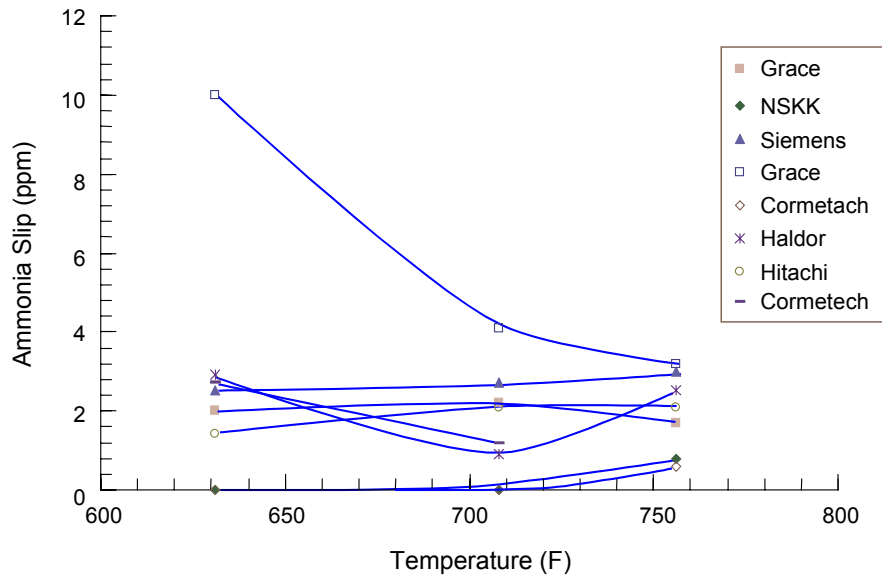
20

Figure 5. SO₂ Oxidation Versus Temperature

620 °F, high flow
Second parametric data set

Figure 6. Ammonia Slip Versus NH₃/NOₓ Ratio

Figure 7. Ammonia Slip Versus Temperature

Significance of Test Results

The test data show that the SCR process can achieve high levels of NO_X reduction while meeting acceptable NH_3 slip levels over an extended period of operation (at least 2 years). In practice, SCR reactors are designed not just to meet a specified NO_X level at startup, but sufficient catalyst volume is provided to allow for catalyst deactivation. This is normal practice in the design of any catalytic reactor, and is not unique to SCR.

NO_X reduction is controlled for the most part by the NH_3/NO_X ratio. Therefore, even with excess catalyst in the reactor, NO_X reduction remains essentially constant over the life of the catalyst. Ammonia slip increases somewhat over time until it reaches the design limit, at which point fresh catalyst is added. In this study, a high NH_3 slip was observed at high levels of NO_X reduction, very likely resulting from the difficulty in precisely measuring and controlling NH_3 flow as well as the maldistribution (i.e., poor mixing) of NH_3 and NO_X. Both issues become critical when operating at NH_3/NO_X ratios that approaches 1.0.

SO_2 oxidation is much more temperature sensitive than NO_X reduction. It can be minimized by controlling operating temperature, and is a function of catalyst formulation by the vendor. The optimum temperature will vary from catalyst to catalyst.

III.4   Boiler Impacts

Operation of the SCR test unit, which treated a slipstream of flue gas downstream of the boiler, had no effect on boiler performance. In commercial practice, the presence of an SCR unit can affect boiler operation insofar as rate of ramping is concerned, since careful temperature control must be maintained at all times.

III.5   Commercialization of the Technology

Current Status

With the completion of the SCR test program at Plant Crist, the experimental facility was dismantled. In view of present and future environmental regulations, several U.S. companies have decided to use SCR on coal-fired utility boilers.

At present, there are six such installations, summarized in Table 5. One of these units, Birchwood, is an independent power producer jointly owned by Southern Energy, Inc. (SEI) and Cogentrix. SEI is a non-regulated subsidiary of Southern Company. The Birchwood SCR design considered data and operational lessons learned from the test program at Plant Crist as valuable input for specifying the process equipment. Since all of the U.S. installations are relatively new, there has not been sufficient time to evaluate long-term performance, particularly with respect to catalyst deactivation. All of the boilers operate on low- to medium-sulfur coals; five of the SCR units are associated with new plants, and one is a retrofit. All of the units are hot-side, high-dust installations.

The U.S. SCR units are achieving NO_X reductions ranging from 56 to 71 percent, depending on the uncontrolled NO_X concentration and the desired level of NO_X in the stack gas. With the exception of one unit that appears to have initially contained insufficient catalyst, there have been few problems in meeting NH_3 slip requirements, and catalyst deactivation has proceeded as predicted from the Plant Crist test data. The poorly performing unit initially experienced frequent plugging of the air preheater surfaces downstream of the SCR reactor. This problem was remedied by installing additional catalyst, which brought performance to the desired level. In general, the plant staff and management at each facility are pleased with the SCR operation, although at least some periodic washing of APHs has been necessary.

Future Work

Although SCR is now being used on coal-fired boilers in the United States, it is expected that design improvements will be made as operating experience is gained. SCR appears to be applicable to all types of boilers. The degree to which SCR will be incorporated in new or future retrofit applications will depend on the severity of NO_X control standards yet to be promulgated.

Table 5. Commercial SCR Installations on Coal-Fired Utility Boilers in the U.S.

Plant	Birchwood	Stanton (Unit 2)	Carneys Point	Logan	Indiantown	Merrimack (Unit 2)
Owner/ Operator	SEI [a]/ Cogentrix	Orlando Utilities Commission	USGen [b]	USGen [b]	USGen [b]	Public Service of NH
Location	King George County VA	Orlando FL	Carneys Point NJ	Swedesboro NJ	Indiantown FL	Concord NH
Capacity, MWe (net)	220	425	260	225	330	330
Export Steam, lb/hr	75,000	--	1,000,000	50,000	125,000	--
Steam Host	Dominion Growers	--	DuPont	Monsanto	Caulkins Citrus	--
Coal Source	WV	KY	PA	WV	KY	?
Coal Sulfur, wt%	1.0	1.1-1.2	<2.0	<1.5	0.8	1.5
Boiler Mfg	ABB/CE	B&W	F/W	F/W	F/W	B&W?
Boiler Type	T-fired	Wall-fired	Wall-fired	Wall-fired	Wall-fired	Wet bottom
Burner Type [c]	LNB/OFA	LNB/OFA	LNB/OFA	LNB/OFA	LNB/OFA	Cyclone
SCR Installation	Hot side, high dust	Hot side, high dust	Hot side, high dust	Hot side, high dust	Hot side, high dust	Hot side, high dust
SCR Catalyst Mfg	Siemens	Siemens	IHI [d]	Siemens	Siemens	Siemens
Catalyst Type	Plate	Plate	Honeycomb	Plate	Plate	Plate
SCR Inlet NO_X, lb/ 10^6 Btu	0.17	0.32	0.32	0.35	0.25	2.66
SCR Outlet NO_X, lb/ 10^6 Btu	0.075	0.17	0.13	0.14	0.15	0.77
NO_X Reduction, %	56	47	59	60	40	71
NH_3 Slip, ppm	<5	2	<5	<5	<5	<2
SCR Pressure Drop, in. H_2O	6	?	<1.0	0.8	Not measured	Not measured
Date SCR Commercial	11/96	6/96	3/94	9/94	12/95	5/95
Carbon on Fly Ash, wt %	?	6-7	15-17 (9-10)?	18-22	15-20	-- [e]
SCR New/ Retrofit	New	New	New	New	New	Retrofit
NH_3 for SCR	Anhydrous	Anhydrous	Aqueous	Aqueous	Aqueous	Anhydrous

[a] Southern Energy, Inc.; [b] U.S. Generating Company, a Pacific Gas and Electric Company/Bechtel partnership; [c] LNB = Low-NO_x burners; OFA = overfire air; [d] Ishikawajima-Harima Heavy Industries; [e] Fly ash recycled to boiler

IV   Market Analysis

IV.1   Potential Markets

The SCR process is applicable to all types of conventional coal-fired boilers, including stoker, cyclone, wall-fired and tangentially fired boilers. As an indication of the potential market for SCR in the U.S., Table 6 lists the boiler population in the Ozone Transport Assessment Group (OTAG) region.

Table 6. Boiler Population in the OTAG Region

Boiler Type	Number of Units	Generating Capacity, MWe
Wall-fired	315	94,327
Tangentially fired	315	112,000
Cyclone	77	22,329
Cell-fired	33	24,143
Wet-bottom	23	4,712
Roof-fired	29	3,111
Total	792	260,622

OTAG, which was created by EPA for the purpose of developing recommendations for ozone reduction, comprises 37 contiguous states, omitting the 11 westernmost states. Many boilers in the OTAG region are candidates for SCR, although regulations are still being formulated and many of these boilers may not be subject to NO_X emissions limits stringent enough to require the use of SCR technology. In any given case, the economic viability of SCR will depend on retrofit difficulty and other site-specific factors.

The need for SCR will be dictated by power plant NO_X emissions limits now being considered, since LNBs, with or without overfire air (OFA), may not be able to meet the lower NO_X target levels. Utilities subject to the most stringent requirements may be forced to use SCR, either alone or in conjunction with LNBs.

IV.2   Economic Assessment of Utility Boiler Applications

SCR Costs — Southern Company Estimates

Southern's final report includes economic estimates for the SCR process. The base case is a 250 MWe greenfield unit, using a projected process design for the nth plant, which incorporates improvements based on experience gained from the demonstration project. The

boiler is either a wall-fired or tangentially fired unit, equipped with LNBs. The coal feed is assumed to contain 2.5 wt% sulfur. The design NO_X concentration at the reactor inlet is 0.35 $lb/10^6$ Btu. NO_X reduction in the SCR unit is assumed to be 60 percent, yielding an outlet concentration of 0.14 $lb/10^6$ Btu. Catalyst deactivation is assumed to be 20 percent at 16,000 hr; that is, the k/k_o ratio is 0.8 at that time. The catalyst price is $400/cu ft.

The estimated capital cost is $54/kW. For a 30-year project life, the levelized cost on a current dollar basis is 2.57 mills/kWh. This is equivalent to $2,500/ton of NO_X removed. On a constant dollar basis, the levelized cost is 1.85 mills/kWh, equivalent to $1,802/ton of NO_X removed. Table 7 summarizes the performance and cost data.

Table 7. Summary of Performance and Cost Data, 1996 Dollars

	Units	Value
Coal Properties		
Higher Heating Value (HHV)	Btu/lb	12,500
Power Plant Attributes With Controls	MWe	250
Plant Capacity, Net	10^9 kWh/yr	1.34
Power Produced, Net	%	65
Capacity Factor	10^6 tons/yr	0.54
Coal Fed		
NO_X Emissions Control Data		
Removal Efficiency	%	60
Emissions Without SCR	$lb/10^6$ Btu	0.35
Emissions With SCR	$lb/10^6$ Btu	0.14
NO_X Removed	tons/yr	1,374
Total Capital Requirement	$/kW	54

	Levelization Factor (a)	mills/kWh	$/ton NO_X Removed
Levelized Cost, Current $			
Capital Charge	0.150	1.50	1,464
Fixed O&M	1.362	0.32	310
Variable O&M	1.362	0.75	726
Total		**2.75**	**2,500**
Levelized Cost, Constant $			
Capital Charge	0.116	1.16	1,132
Fixed O&M	1.000	0.23	228
Variable O&M	1.000	0.46	442
Total		**1.85**	**1,802**

Obviously, the economics are highly dependent on a number of variables, including plant

capacity, degree of NO_X removal, and inlet NO_X concentration. Southern's economic analysis includes the effects of these variables, summarized in Table 8 below. Levelized costs are on a current dollar basis.

Table 8. Effects of Variables on SCR Performance

Capacity, MWe	125	250	700
NO_X Removal, %	60	60	60
Inlet NO_X, lb/10^6 Btu	0.35	0.35	0.35
Capital, $/kW	61	54	45
$/ton NO_X removed	2811	2500	2165
Capacity, MWe	250	250	250
NO_X Removal, %	**40**	**60**	**80**
Inlet NO_X, lb/10^6 Btu	0.35	0.35	0.35
Capital, $/kW	52	54	57
$/ton NO_X removed	3502	2500	2036
Capacity, MWe	250	250	250
NO_X Removal, %	60	60	60
Inlet NO_X, lb/10^6 Btu	**0.45**	**0.35**	**0.25**
Capital, $/kW	54	54	54
$/ton NO_X removed	1977	2500	3446

At a given plant capacity, levelized costs ($/ton of NO_X removed) decrease with an increasing NO_X removal rate and increasing initial NO_X concentration, such as would occur in situations where SCR is used on boilers with the highest uncontrolled NO_X levels and without combustion modification. Not shown in the above table is the effect of catalyst deactivation. Longer catalyst life, reduced catalyst prices, or both would reduce costs. Retrofit costs can be significantly greater, especially in cases involving difficult reactor siting and duct arrangements, new fans, and balanced draft conversions. In one case, the estimated capital cost was $130/kW, representing $65/kW for the SCR unit and $65/kW for conversion to balanced draft operation.

Because of the relatively high capital costs involved, some companies are investigating innovative business arrangements for implementing SCR projects.

SCR Costs — Commercial Installations

Costs for recent U.S. commercial applications of SCR have been obtained for two power plants: the Stanton Energy Center (Unit 2) in Florida, and the Merrimack (Unit 2) in New Hampshire. At Stanton, which was a new installation having a capacity of 425 MWe net and a NO_X removal efficiency of 47 percent, the capital cost was $14 million, which is equivalent to $33/kW. At Merrimack, which was a retrofit installation having a capacity of 330 MWe net and a NO_X removal efficiency of 71 percent, the capital cost was $18.5 million, which is equivalent to $56/kW. To compare these capital costs with those developed by Southern would require more detailed information on the scope of work involved. For both plants, operating costs consist primarily of NH_3 reagent expense and catalyst replacement. According to management at those two plants, additional labor or maintenance costs incurred by the SCR units are minimal.

Comparison With Other Technologies

NO_X reduction sufficient to meet Title IV requirements is currently being achieved by combustion modification, which includes LNBs and fuel reburning. To reach deeper reductions in NO_X emissions as proposed in the new Title I regulations may require post-combustion processes, which include SCR and selective non-catalytic reduction (SNCR). Since SNCR does not require a catalyst, it is considerably less expensive than SCR. However, typical demonstrated NO_X removal for SNCR ranges from about 25 to 40 percent, which is much lower than with SCR. In addition, some experience has shown that SNCR applications are limited to smaller boilers because of difficulties in achieving uniform distribution of reagent in the flue gas stream. Numerous control problems have arisen especially where loads fluctuate. Therefore, SCR may be preferred over SNCR in some situations. Hybrid processes, using SNCR followed by SCR, have the potential for operating flexibility at lower overall cost. Such configurations need to be evaluated on a case-by-case basis.

V Conclusions

The SCR demonstration project was successful: all objectives were met. All eight catalysts in the test program met design specifications, providing at least 80-percent NO_X removal at an NH_3 slip of 5 ppm or less. Although the catalysts varied somewhat in operating characteristics, such as activity and pressure drop, no one catalyst was found to be superior. Catalyst deactivation proceeded as expected based on European and Japanese experience, with an average decrease in activity of 20 percent over a 2-year period. Although no unusual deactivation effects could be attributed to the use of high-sulfur U.S. coals containing typical concentrations of metals such as arsenic, there is uncertainty regarding the required frequency of catalyst replacement. Both plate and honeycomb catalysts performed satisfactorily.

There was significant variation in the rate of oxidation of SO_2 to SO_3 among the catalysts tested. Sufficient amounts of $(NH_4)_2SO_4$ and NH_4HSO_4 were formed to result in corrosion and plugging of the APHs, requiring periodic washing. The overall stability of the pressure drop across the catalysts over time indicated that the soot-blowing procedures used in the test program were satisfactory. Performance comparisons between high-dust and low-dust reactor configurations were inconclusive because of problems associated with the design of the low-dust reactor.

A commercial scale SCR unit can be installed for about $54/kW in a new plant. Retrofit costs could be significantly higher. Six commercial SCR units are operating on low- and medium-sulfur coals in the United States. A significant market for SCR exists in the United States, especially in light of increasingly stringent limitations on NO_X emissions. Design improvements can be expected as operating experience is gained, and application to other boilers can be anticipated.

VI   Abbreviations and Acronyms

APH	air preheater
BACT	best available control technologies
CAAA	Clean Air Act Amendments
CCT	Clean Coal Technology Program
DOE	U.S. Department of Energy
EPA	U.S. Environmental Protection Agency
EPRI	formerly the Electric Power Research Institute
ESP	electrostatic precipitator
LNBs	low NO_X burners
NAAQS	National Ambient Air Quality Standards
NH_3	ammonia
$(NH_4)_2SO_4$	ammonium sulfate
NH_4HSO_4	ammonium bisulfate
NOTR	Northeast Ozone Transport Region
NO_X	nitrogen oxides
NSPS	New Source Performance Standards
OFA	overfire air
OTAG	Ozone Transport Assessment Group
RACT	reasonably available control technology
SCR	selective catalytic reduction
SNCR	selective non-catalytic reduction
SEI	Southern Energy Inc.
SIP	State Implementation Plan
SO_2	sulfur dioxide
SO_3	sulfur trioxide
T-fired	tangentially fired
VOCs	volatile organic compounds

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