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**DEVELOPMENT OF THE
INTEGRATED ENVIRONMENTAL CONTROL MODEL:
PERFORMANCE MODELS OF SELECTIVE CATALYTIC REDUCTION
NO_x CONTROL SYSTEMS**

Quarterly Progress Report

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U.S. Department of Energy
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from

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Introduction

The purpose of this contract is to develop and refine the Integrated Environmental Control Model (IECM) created and enhanced by Carnegie Mellon University (CMU) for the U.S. Department of Energy's Pittsburgh Energy Technology Center (DOE/PETC) under contract Numbers DE-FG22-83PC60271 and DE-AC22-87PC79864.

In its current configuration, the IECM provides a capability to model various conventional and advanced processes for controlling air pollutant emissions from coal-fired power plants before, during, or after combustion. The principal purpose of the model is to calculate the performance, emissions, and cost of power plant configurations employing alternative environmental control methods. The model consists of various control technology modules, which may be integrated into a complete utility plant in any desired combination. In contrast to conventional deterministic models, the IECM offers the unique capability to assign probabilistic values to all model input parameters, and to obtain probabilistic outputs in the form of cumulative distribution functions indicating the likelihood of different costs and performance results.

The most recent version of the IECM, implemented on a Macintosh II computer, was delivered to DOE/PETC at the end of the last contract in May 1991. The current contract will continue the model development effort to provide DOE/PETC with improved model capabilities, including new software developments to facilitate model use and new technical capabilities for analysis of environmental control technologies. Integrated environmental control systems involving pre-combustion, combustion, and post-combustion control methods will be considered.

The work in this contract is divided into two phases. Phase I deals with further developing the existing version of the IECM and training PETC personnel on the effective use of the model. Phase II deals with creating new technology modules, linking the IECM with PETC databases, and training PETC personnel on the effective use of the updated model.

The present report summarizes recent progress on the Phase I effort during the period April 1, 1993 through June 30, 1993. This report summarizes our progress to date in refining the existing analytical model of selective catalytic reduction (SCR) technology for NO_x control. This report presents a new performance model for SCR systems based on recent experience. A future report will present the companion economic model, still under development.

1.0 Introduction to SCR Technology

Selective catalytic reduction (SCR) is a process for the post-combustion removal of NO_x from the flue gas of fossil-fuel-fired power plants. SCR is capable of NO_x reduction efficiencies of up to 80 or 90 percent. SCR technology has been applied for treatment of flue gases from a variety of emission sources, including natural gas- and oil-fired gas turbines, process steam boilers in refineries, and coal-fired power plants. SCR applications to coal-fired power plants have occurred in Japan and Germany. Full-scale SCR systems have not been applied to coal-fired power plants in the U.S., although there have been small-scale demonstration projects.

Increasingly strict NO_x control requirements are being imposed by various state and local regulatory agencies in the U.S. These requirements may lead to U.S. SCR applications, particularly for plants burning low sulfur coals (Robie et al., 1991). Furthermore, implicit in Title IV of the 1990 Clean Air Act Amendment is a national NO_x emission reduction of 4 million pounds per year. Thus, there may be a strong incentive to adapt SCR technology more generally to U.S. coal-fired power plants with varying coal sulfur contents. However, concern remains over the applicability of SCR technology to U.S. plants burning high sulfur coals or coals with significantly different fly ash characteristics than those burned in Germany and Japan. There is also concern regarding the application of SCR to peaking units due to potential startup and shutdown problems (Lowe et al., 1991).

In this report, the process history of SCR is reviewed. Technical background information is used to provide a basis for the development of performance models of two alternative SCR systems for NO_x control of coal-fired power plants. These are "hot-side high-dust" and "tail-end low-dust" options.

2.0 Process History and Development

SCR was invented and patented in the U.S. in 1959. It was used originally in industrial applications. In the 1970's, SCR was first applied in Japan for control of NO_x emissions from power plants. Japan was the first country to make widespread use of this technology in response to national emission standards for NO_x . In Japan, SCR has been applied to gas, oil, and coal-fired power plants. There were over 200 commercial SCR systems operating on all types of sources in Japan in 1985. The Japanese SCR systems tend to run at moderate NO_x removal efficiencies of 40 to 60 percent (Gouker and

Brundrett, 1991). By 1990, a total of 40 systems had been installed on 10,852 MW of coal-fired power plants (Lowe et al., 1991).

The Federal Republic of Germany currently imposes more stringent NO_x emission standards than Japan. To meet the emission requirements, SCR has been adopted and applied to many coal-fired power plants. SCR will be required as a retrofit technology on a total of 37,500 MW of existing capacity. As of 1989, SCR had been applied in 70 pilot plants and 28 full scale retrofit installations, with the latter totalling 7,470 MW of hard coal-fired capacity (Schönbucher, 1989). By 1990, more than 23,000 MW of capacity were fitted with SCR systems (Gouker and Brundrett, 1991). These plants typically burn low sulfur coals (0.8 to 1.5 percent sulfur) with 0.1 to 0.3 percent chlorine. SCR has been retrofitted to power plants with both wet and dry bottom boilers, with variations on the location of the SCR system. As of 1989, 18 installations involve placement of the SCR system between the economizer and air preheater, while the remaining involve "low dust" or "tail-end" placement of the SCR downstream of the FGD system. Two of the high-dust retrofits involve wet bottom boilers (Schönbucher, 1989). In 1991, 129 systems were reported to have been installed on a total of 30,625 MW of coal-fired capacity (Lowe et al., 1991). The recent German progress in installing retrofit SCR systems is shown graphically in Figure 1.

The process environment for SCR in Germany is typically more demanding than that in Japan, with the requirement for higher NO_x removal efficiencies in the presence of higher flue gas sulfur and ash loadings (Gouker and Brundrett, 1991). In both Japan and Germany, the SCR systems are not operated during startup or shutdown (Lowe et al., 1991).

SCR is being applied in the U.S. for NO_x control of natural gas and oil-fired gas turbine-based power generation systems. In 1990 SCR was installed at a total of 110 gas turbine units totalling 3,600 MW (May et al, 1991). While the operating environment for these systems is not as demanding as for coal-fired power plant applications, some of these applications do provide experience with systems firing sulfur-bearing fuels that encounter problems analogous to those anticipated in coal-based applications. In particular, ammonium salt formation and downstream effects have been studied (Johnson et al, 1990).

Recently, a number of U.S. projects for coal-fired applications of SCR technology have been initiated. These include, for example, a U.S. Department of Energy Clean Coal Program funded demonstration of SCR at Gulf Power Company's Plant Crist (DOE,

Figure 1. Targeted and Actual Installed Retrofit SCR Capacity in Germany

1992). SCR systems have also been permitted for two coal-fired cogeneration plants to be built in New Jersey (Fickett, 1993).

Since the 1970's, the cost of SCR has dropped substantially. For example, the levelized cost of SCR dropped by a factor of 3 in Japan within a 6 year period, while in recent years costs in Germany have dropped by an additional factor of 2. These improvements are due in part to the international competition among catalyst suppliers. SCR catalysts are available from manufacturers in Japan, Germany, and the U.S. U.S. manufacturers, such as Grace, expect improvements in catalysts to continue, resulting in potential further drops in capital and operating costs. For example, Grace is testing a new catalyst design which is expected to lead to a 50 percent increase in catalyst activity while also increasing catalyst life (Gouker and Brundrett, 1991).

SCR has not yet been used commercially on coal-fired power plants in the U.S. The experience in Germany, which includes boiler types similar to those in the U.S., provides useful data for predicting SCR performance and cost in the U.S. However, U.S. coals, such as eastern bituminous coals, typically have a higher sulfur content than that of German coals. In addition, fly ash compositions may vary significantly. These differences lead to concerns about maintenance of catalyst activity and potential difficulties downstream of SCR reactors, such as deposition of ammonia salts.

The German experience is particularly useful for U.S. planners because German SCR systems are subject to a more relevant range of flue gas conditions than typical Japanese systems. For example, slagging wet bottom boilers produce different flue gas and flyash characteristics that can significantly affect catalyst performance (Offen et al, 1987).

3.0 Process Design

The general design considerations for the SCR NO_x control technology for coal-fired power plants are described here. These include the placement of the SCR system in a power plant, and a description of equipment associated with the SCR process area.

3.1 SCR Integration in the Power Plant

The SCR system can be located in several places in the coal-fired power plant flue gas stream (Schönbucher, 1989; Behrens et al, 1991). A key limitation of SCR systems is the operating temperature requirement. The operating temperature window for SCR systems is typically from approximately 550 to 750 °F. Several possible locations are illustrated in Figure 2. These are:

- a) "Hot-side" and "high-dust" SCR, with the reactor located between the economizer and the air preheater. In this configuration, shown in Figure 1(a), the SCR is located upstream of a cold-side ESP and, hence, is subject to a high fly ash or "dust" loading. At full-load, the economizer outlet temperature is typically around 700 °F. An economizer bypass is required to supply hot gas to the SCR during part-load operating conditions, in order to maintain the proper reaction temperatures (Lowe et al, 1991).
- b) "Hot-side, low-dust" SCR, which features placement of the SCR system downstream of a hot-side ESP and upstream of the air preheater and FGD systems. This configuration has been employed in some Japanese coal-fired power plants, such as Takehara Power Station Unit 1 in Hiroshima (Behrens et al, 1991). This configuration has the advantage of minimizing the fly ash loading to the SCR catalyst, which leads to degradation in catalyst performance.
- c) "Cold-side" or "Tail-end" placement of the SCR system downstream of the air preheater, particulate collector, and FGD system. This system minimizes the effects that flue gas contaminants have on SCR catalyst design and operation, but requires a gas-gas flue gas heat exchanger and duct burners to bring the flue gas up to reaction temperature (Lowe et al, 1991).

The most common configurations envisioned for U.S. power plants are the hot-side high-dust and post-FGD tail-end systems (Robie et al, 1991), with high-dust systems predominating. These are the two most common configurations employed in German coal-fired power plants retrofitted with SCR.

Recent German experience indicates increasing acceptance for tail-end systems. Prior to 1987, the number of high-dust installations was twice that of tail-end installation. But since 1987, the number of tail-end installations has been slightly greater. The tail-end

(a) Hot-side, high dust configuration

(b) Hot-side, low-dust configuration

c) Tail-end configuration

Figure 2. Alternative Placements of SCR Systems in Coal-Fired Power Plants.

systems have tended to be installed on smaller plants, however, and account for about one-third of total installed capacity. They have been preferred for wet bottom boiler applications (Lowe et al, 1991).

In many evaluations, tail-end SCR systems have been charged with the full cost of flue gas reheat, even though a portion of the reheat would be necessary to maintain stack buoyancy for flue gas exiting the FGD system. Similarly, in comparing hot-side and tail-end systems, the significant efficiency penalty for the high-dust system when operating at part load, due to the need for economizer bypass, must be considered (Lowe et al, 1991).

3.2 The SCR Process Area

A schematic of the SCR system is given in Figure 3. The schematic assumes an SCR location in the hot-side, high-dust configuration. Ammonia is injected into the flue gas upstream of the SCR reactor vessel. The ammonia/flue gas mixture enters a reactor vessel, containing SCR catalyst. The catalyst promotes the reaction of ammonia and NO_x to form nitrogen and water vapor. Products of the SCR reactions may form ammonium sulfate or bisulfate, which can deposit on downstream equipment. Additional air preheater water washing is expected to be required to remove such deposits.

The SCR system consists primarily of a reactor housing containing catalyst material, an ammonia storage and handling system, an ammonia injection system, and a control system. In addition, air preheater wash water pretreatment may be required to remove ammonia from the wastewater.

A more detailed schematic of the SCR reactor housing is shown in Figure 4. SCR design philosophy has evolved over the last 20 years due to the accumulation of operating experience in Japan and Germany. Based on Japanese experiences, both vendors and users of SCR technology have identified the following key design considerations for hot-side SCR systems (Lowe et al, 1991):

- Vertical downward flue gas flow to prevent ash accumulation and to allow ash drop out.
- Linear gas velocities of 16-20 ft/sec at maximum continuous rating to prevent ash accumulation. Higher velocities would be expected to increase catalyst erosion.
- Use of grid shaped catalyst with channel spacing (pitch) of 7 to 7.5 mm to allow passage of dust and prevent ash accumulation and erosion.
- Elimination of catalyst seams along the gas flow direction to prevent ash accumulation and erosion.

Figure 3. Schematic Diagram of SCR System

Figure 4. Diagram of SCR Reactor Housing with Downward Flue Gas Flow

- Use of a "sacrificial" or dummy initial stage to prevent ash accumulation and erosion in downstream active catalyst layers.
- Removal of deposited ash using intermittent vacuuming or soot-blowing.
- Reliable ammonia feed control, including part load operation.
- Adequate ammonia feed distribution across the cross sectional flue gas flow area.
- Flue gas ducting and guide vane designs that ensure good mixing of the flue gas and ammonia feed.

Most of these features are illustrated in Figure 4.

A tail-end SCR system is illustrated in Figure 5 to show the configuration of the gas-gas heat exchanger and duct burner. The flue gas exiting the FGD system must be heated from approximately 130 °F to a reaction temperature of approximately 625 °F. The flue gas exiting the SCR can be cooled to a stack temperature near 225 °F. Flue gas from the FGD system is preheating with flue gas exiting the SCR system in a heat exchanger. The SCR inlet flue gas is then heated to reaction temperature using a duct burner.

3.2.1 Catalyst

SCR catalysts typically consist of a ceramic honeycomb substrate, a metal "carrier" and active components dispersed by the carrier on the honeycomb surfaces. A typical carrier is titanium dioxide (TiO_2). Vanadium pentoxide (V_2O_5) and tungsten trioxide (WO_3) are commonly used as active components for hot-side SCR applications (Schönbucher, 1989). WO_3 provides thermal and mechanical stability to the catalyst (Behrens et al, 1991). Catalysts based on titanium dioxide are best suited for operating temperatures of 280 to 400 °C (536 to 752 °F) (Schönbucher, 1989). At lower temperatures, catalyst activity drops substantially. At higher temperatures, catalyst material phase transition occurs, which causes irreversible activity loss (Bauer and Spendle, 1984). Catalysts using activated carbon may be employed for lower temperature applications near 100 °C (212 °F) (Schönbucher, 1989). The actual catalyst formulations which are offered commercially are closely held propriety information.

A key innovation from Japanese development of SCR technology has been the switch from noble metal oxides to base metal oxides for use as catalyst carrier materials, which has reduced many of the major problems associated with oil- and gas-fired flue gas applications. For coal applications, Japanese catalyst development also focused on improving catalyst geometry. To avoid plugging and erosion, parallel flow honeycomb and plate catalysts were developed. By the early 1980's, ceramic honeycomb and plate configurations have been developed that provide high surface areas while reducing the

Figure 5. Schematic Diagram of Tail-End SCR System

tendency for flyash plugging. In recent years, research has focused on understanding the deactivation mechanisms of SCR catalyst, particularly due to alkalis and trace metals such as arsenic (Gouker and Brundrett, 1991).

V_2O_5 is the component which controls the reactivity of the catalyst. However, it also catalyzes the conversion of SO_2 to SO_3 (Behrens et al, 1991), which may lead to opacity, ammonium salt deposition, or acid condensation problems downstream. For high-sulfur coal applications, the amount of V_2O_5 is minimized by homogeneous distribution throughout the catalyst. To obtain NO_x reduction, properly mixed ammonia and NO_x must enter micropores in the catalyst, which are the active sites for the reactions which consume NO_x .

The catalyst is typically installed in a reactor housing in three layers, with provision for a dummy layer for flow straightening and distribution. In some designs, provision is also made for a fourth active catalyst layer. In these cases, the initial catalyst charge consists of three active layers. When catalyst activity drops to the design value, a fourth active layer is added. Then the four layers are changed out periodically to maintain overall catalyst activity. Catalyst modules may be loaded and unloaded from the reactor housing using a fork-lift track assembly and/or rollers (e.g., Behrens et al, 1991)

Ceramic, homogeneous, honeycombed catalyst elements approximately 6 inches square can be extruded to a length of about 39 inches (Behrens et al, 1991). SCR systems subject to high-dust loadings often include a dummy honeycomb or leading edge to control catalyst erosion (Lowe et al, 1991). Catalyst honeycomb design depends on the location of the SCR system in the power plant. For high-dust systems, catalysts with a large pitch (spacing within honeycomb cells) are employed, to allow passage of fly ash. For low dust systems, smaller pitch catalysts can be used (Schönbucher, 1989). These catalyst designs are illustrated in Figure 6.

3.2.2 Ammonia Handling

In Germany, strict safety standards have been applied to the shipment and handling of ammonia. Shipments by truck are not permitted if they are larger than 500 liters. Thus, anhydrous ammonia is shipped primarily by rail. A 15 to 30 day supply is typically stored at the plant in two double wall tanks. Double walled piping is also typically employed. The ammonia is diluted to an 8 percent mixture prior to introduction to the flue gas. The ammonia is vaporized in German facilities using warm water. In many U.S. gas turbine installations, electrical heating is used (Lowe et al, 1991).

(a) Monolith for High-Dust Application

(b) Monolith for Tail-End Application

Figure 6. SCR Honeycomb Catalyst Monolith Designs

4.0 Technical Overview

This section presents a detailed technical overview of SCR NO_x control technology for coal-fired power plants, with particular focus on the effects of flue gas components on catalyst performance and the effects of the SCR system on the power plant.

4.1 Process Chemistry

Nitrogen oxides in the flue gas are removed by reduction of NO_x by ammonia to nitrogen and water. The reduction occurs in the presence of a catalyst. Ammonia is injected in the flue gas upstream of the catalyst, as illustrated previously in Figure 3.

The principle reactions are:

Of these reactions, reaction (3) is usually the most important. There is usually sufficient oxygen in the flue gas as a reactant. In addition, typically 90 to 95 percent of nitrogen oxides in the flue gas are in the form of NO.

Another overall reaction that may occur in the SCR unit is (Anderson and Billings, 1991):

The implication of the above reaction is that a molar ratio of ammonia to NO_x of 1:1 is sufficient to remove both NO and NO_2 when the NO/ NO_2 mixture contains more than 50 percent NO.

Another important reaction occurring in the SCR reactor is the oxidation of sulfur dioxide:

Typically, 0.5 to 2 percent of the sulfur dioxide entering the SCR reactor is oxidized to sulfur trioxide (e.g., Bauer and Spendle, 1984). The resulting increased levels of sulfur trioxide at the SCR outlet increases the acid dewpoint of the flue gas, thus increasing the potential for sulfuric acid condensation on downstream components at temperatures of less than about 350 °F. Sulfur trioxide may react with water vapor to form sulfuric acid (Johnson et al, 1990):

where subscripts (g), (l), and (s) represent gas, liquid, and solid phases, respectively.

Unreacted ammonia exiting the SCR system ("ammonia slip") can react with sulfur trioxide to form compounds such as ammonium bisulfate and ammonium sulfate that deposit on downstream equipment. These compounds may result in plugging and corrosion. The key reactions for the formation of ammonium sulfate and bisulfate are (Johnson et al, 1990):

The formation of ammonium bisulfate (Equation (9)) is more sensitive to sulfur trioxide concentration than to ammonia concentration (Lowe et al, 1991).

As the flue gas cools in downstream equipment, the sulfuric acid may also react with ammonia to form condensate products (Johnson et al, 1990):

The formation of ammonium bisulfate and other ammonia salts can be minimized by reducing the ammonia slip and reducing the formation of sulfur trioxide.

The key design considerations for SCR are the NO_x removal efficiency, the ammonia slip, and the SO_2 oxidation rate. While larger catalyst volumes allow higher NO_x removal efficiencies and/or lower ammonia slip, they tend to increase the oxidation of SO_2 . Furthermore, large catalyst volumes significantly increase the capital and annual costs of SCR.

4.2 Catalyst Sizing

A key performance issue associated with SCR systems is the required catalyst volume and the catalyst replacement schedule. One parameter often used to measure catalyst volume is the space velocity, which is given by:

$$\text{SV} = G_{\text{FG}}/V_c \quad (12)$$

An alternative parameter is the area velocity, which is given by:

$$\text{AV} = G_{\text{FG}}/V_c \quad (13)$$

The relationship between the space velocity and area velocity depends on the "geometric ratio" of the catalyst, which is the unit surface area per unit volume of the catalyst.

$$R_g = \frac{A_c}{V_c} \quad (14)$$

For honeycomb monolith catalysts, the important design parameter that determines the geometric ratio is the "pitch," or spacing between the hollow cells through which the flue gas passes. As described in Section 3.2, the catalyst pitch depends primarily on the dust loading in the flue gas. Larger pitches are needed to accommodate high-dust loadings, resulting in a lower geometric ratio. Current catalysts for high-dust application typically have a pitch of around 7.5 mm, with a wall thickness of 1.4 mm and a channel thickness of 6.1 mm. For tail-end applications, pitches of around 4 mm are typical. For gas-fired applications, pitches of 3 mm are reported using ceramic plate-type catalysts. Catalyst

using thin metal substrates may have a pitch as low as 0.2 mm for clean flue gas applications (Gouker and Brundrett, 1991).

The space velocity is commonly used to describe the catalyst requirement. However, both the space velocity and area ratio, or the space and area velocities, are needed in order to specify both the catalyst volume and the catalyst area in contact with the flue gas. For example, a high-dust SCR system typically requires a smaller space velocity (more catalyst) than a low-dust system, due primarily to the lower area ratio of the high-dust catalyst designs.

The space velocity is a function of the desired NO_x removal efficiency and the required ammonia slip. For example, one EPRI paper suggests a maximum space velocity of 2,500/hr for a NO_x reduction efficiency of 80 percent and an ammonia slip of 5 ppm (Damon et al, 1987).

Based on German experience, typical space velocities for high-dust SCR systems with honeycomb catalysts of about 7 mm pitch are 2,000 to 3,000/hr, whereas for tail-end systems employing honeycomb catalysts with pitches of approximately 4 mm space velocities are 4,000 to 6,500/hr. Thus, 50 to 60 percent smaller catalyst volumes per unit flue gas flow can be installed on tail-end systems for equivalent NO_x removal performance. However, the flue gas volumetric flow rate may be higher for tail-end systems than for high-dust systems, partially offsetting this advantage (Lowe et al, 1991).

The actual required catalyst volume for a given application depends on a number of site-specific factors. The amount of plugging or catalyst poisoning will determine the effective catalyst activity. The activity will decrease with operating time. Therefore, the initial catalyst volume must be large enough so that at the end of the design life there is sufficient active catalyst to maintain design performance levels.

Most SCR designs have a three layer catalyst. Although most U.S. SCR studies assume that all catalyst layers are changed out simultaneously, most Japanese and German designs are based on periodic replacement of only one catalyst layer at a time. Therefore, at any given time, there may be three layers with differing lengths of service and differing activity levels. In determining the initial catalyst charge, it is necessary to account for the loss of catalyst activity at the design point in the catalyst replacement scheme. For a three layer catalyst, the design point is the fourth catalyst change out.

To determine the catalyst activity at the design point, it is necessary to estimate the loss of catalyst activity as a function of time. Catalyst activity loss is a function of the

catalyst formulation and geometry, the operating conditions associated with the flue gas, including temperature and composition, and the loading and composition of the fly ash. Recent papers, such as those presented at the 1991 Symposium on Stationary NO_x Control, provide examples of catalyst activity loss curves for specific power plant applications in Germany (e.g., Behrens et al, 1991; Gouker and Brundrett, 1991; Maier and Dahl, 1991) .

4.3 Catalyst Fouling and Poisoning

Commercial operating experience in both Germany and Japan have provided insight into the mechanisms for catalyst fouling and poisoning. For coal-fired power plant applications, the primary cause of loss of catalyst activity was attributed to interactions between the catalyst and the flyash. As summarized by Gouker and Brundrett (1991), flyash has several effects on the catalyst, including:

- **Fouling:** Sub-micron ash particles may accumulate on the surfaces of the catalyst, and block the pores of the catalyst. This fouling or masking prevents NO_x and ammonia from reaching active catalyst sites, thereby reducing the effective catalyst surface area. This leads to a reduction in the performance of the catalyst.
- **Plugging:** Bulk plugging of the catalyst occurs when large accumulations of dust occur. Dust plugging may occur, for example, when large pieces of flyash on upstream equipment "flake" off. Wire screens located upstream of the catalyst help to break up these flakes. Soot blowing may also be required periodically to remove the flakes from the catalyst.
- **Poisoning:** Alkali metals from flyash are a source of catalyst poisoning. Water soluble alkali salts may be leached onto the catalyst due to moisture present on fly ash during startup or shutdown of the SCR unit. Alkali salts have been shown to form inactive complexes with vanadium and tungsten in laboratory studies.
- **Erosion:** Erosion problems may arise due to flue gas flow distribution problems. Flow straightening vanes and dummy "catalyst" layers have been employed in many installations to reduce this type of problem.

4.3.1 Japanese and German Experience

Due to improvements in catalyst technology, catalysts in Germany are not experiencing as much loss of activity as initially predicted based on Japanese high-dust, coal-fired applications (Gouker and Brundrett, 1991).

Behrens et al (1991) report that the typical levels of potential catalyst poisons in the flyash of Ruhr coal have "not appeared to significantly accelerate catalyst deterioration" of the hot-side high-dust SCR unit at the Reuter West power station. These contaminant levels include 4 to 5 percent K₂O, 6.3 percent of CaO, 1.5 percent of MgO, and 0.6 percent of P₂O₅. However, data reported by them does indicate that catalyst activity decreased to 65 percent of the level of the fresh catalyst after 30,000 hours.

At the Aichi 40 MW coal-fired boiler burning low sulfur coal, a hot-side high-dust SCR arrangement is employed. The catalyst has experienced low deterioration. After 30,000 hours of operating, the catalyst activity is 75 percent of the fresh catalyst. The primary cause of deactivation is reported to be the deposition of CaSi on the catalyst surface (Behrens et al, 1991).

While arsenic is commonly cited as the most significant catalyst poison, small sticky dust particles can cause more serious deactivation than arsenic. Furthermore, in some cases, SCR fires due to dust accumulations have occurred in Japan (Lowe et al, 1991).

German experience with SCR catalyst indicates that catalyst "lifetimes" of 3 to 4 years are possible and typical for high-dust systems. For tail-end systems, some operators report no measurable catalyst degradation, and expect to achieve up to 80,000 operating hours on a single catalyst charge. Japanese experience on clean flue gases has been similar (Lowe et al, 1991).

In many German wet bottom boilers, fly ash is recirculated to the boiler in order to slag the ash. Arsenic tends to concentrate preferentially in the fly ash during this process by 10 to 100 times compared to cases where no fly ash recirculation is used. A study of 14 wet bottom plants indicates that the actual arsenic concentration obtained in the flue gas is not monotonically proportional to the coal arsenic concentration, but may depend also on the calcium content of the flyash. Calcium oxide in the fly ash tends to getter arsenic, leading to higher arsenic concentrations in the fly ash and lower gaseous arsenic concentrations in the flue gas. This reduces the effect of arsenic as a catalyst poison. However, calcium can also "blind" the catalyst, if it does not react with arsenic (or perhaps other species). Hence, for flue gases where arsenic is not present, Japanese experience has been that fly ash calcium oxide contents of less than 1 percent permit long catalyst lives (e.g., 38,000 hours) while higher calcium contents of 5 to 8 percent result in shorter lives of less than 25,000 hours. For high sulfur coals that yield a gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) component in the fly ash, the deactivation of catalyst is less pronounced (Lowe et al, 1991).

4.3.2 Laboratory Studies of Poisons

A laboratory study by Chen et al (1990) examined the effect of several catalyst poisons on a laboratory manufactured sample of 5 percent V_2O_5 catalyst on a TiO_2 carrier. Both catalyst pellets and a ceramic substrate honeycomb catalyst were evaluated. The specific catalyst poisons that were evaluated include five alkali oxides (Li_2O , Na_2O , K_2O ,

Rb₂O, and Cs₂O) and four additional compounds CaO, PbO, P₂O₅, and As₂O₃. In the experimental work, maximum catalyst activity was observed in the 200 to 300 °C (392 to 572 °F) temperature range. Commercial catalysts also include WO₃ as a component, which allows increased catalyst activity at higher temperatures of 300 to 400 °C (572 to 752 °F).

U.S. coals, and especially eastern bituminous coals, contain relatively high concentrations of alkali metals. Thus, the effects of alkali and alkaline earth metal oxides on catalyst are important in these applications. Catalyst activity was shown to decrease as the amount of alkali metal dopant was increased in the laboratory tests. The strength ordering of the alkali oxide poisons corresponds to their basicity, with Cs₂O having the most pronounced effect. The deactivation may occur due to acid-base reactions forming alkali-vanadium compounds (e.g., NaVO₃). The poisoning due to CaO is weaker than that of the alkali metals. The basicity of CaO is also weaker than the weakest alkali oxide tested, Li₂O. Lead oxide, although a strong poison for automobile catalytic converters, is less important than the top three alkali metal oxides in deactivating the catalyst.

Although arsenic is often cited as the major catalyst poison concern, the experimental results of Chen et al (1990) indicate that As₂O₃ is a substantially weaker catalyst poison than the alkali metal oxides Na₂O, K₂O, Rb₂O, and Cs₂O. P₂O₅ was also found to be a relatively weak poison.

However, the poisoning effect of both As₂O₃ and P₂O₅ are temperature dependent, with increased catalyst deactivation at lower temperatures. P₂O₅ poisoning leads to the formation of phosphate on the catalyst surface, which changes the catalyst surface active properties, and the blockage of surface area and pores. In spite of its relatively low poisoning activity, As₂O₃ may be a more notable poison because it is often found in gaseous form, whereas many of the potentially stronger alkali metal oxides are contained in the molten coal ash.

SO₂ entering the SCR reactor is a precursor to the formation of SO₃, ammonium sulfates, and sulfuric acid. Under certain conditions, ammonium sulfate may deposit on the catalyst, leading to catalyst deactivation. However, SO₂ alone has shown a promoting effect on catalyst activity. Formation of surface sulfates on the catalyst may promote the acidity of the surface. The work of Chen indicates that poisoning is associated with increasing basicity of the catalyst due to other contaminants.

Chloride species may have either poisoning or promoting effects on the catalyst. The poisoning effects of chlorides are much weaker than those of the corresponding oxides

of the same metals (e.g., NaCl and Na₂O). In fact, the chlorine atom has a promoting effect, while the alkali metal atom has a poisoning effect, with a net poisoning for NaCl and KCl. KCl is a stronger poison than NaCl, analogous to the metal oxide K₂O being stronger than Na₂O.

HCl appears to react with ammonia to form NH₄Cl, which consumes ammonia and reduces ammonia available for NO_x conversion. It also deposits on the catalyst at temperatures below 340 °C (644 °F). HCl also appears to react with lower vanadium oxides, which are formed by reduction with ammonia, to form VCl₄ and VCl₂, which are red-brown and green liquids, respectively. Some chlorides, such as Cu₂Cl, act as an SCR catalyst, which may be attributable to its acidity.

In a later study, Chen et al (1991) also added WO₃ to the catalyst formulation, yielding catalyst samples more representative of commercial offerings. They performed a set of tests with the same poisons as described above. WO₃ was found to improve catalyst activity and the resistance of catalyst to poisoning. However, similar qualitative results were obtained. Alkali compounds had the most pronounced effect in proportion to their basicity. Lead, arsenic, and phosphorous were also found to be weaker poisons than the strong alkali compounds tested. The addition of SO₂ decreased the activity of the WO₃ formulation catalyst, although when doped with alkali activity increased. Similar results were obtained for chloride related effects. In cases where vanadium chlorides form, catalyst activity will decrease.

The results of both studies (Chen et al, 1990; Chen et al, 1991) were not intended to identify the interactive simultaneous effects of multiple catalyst poisons in combination with masking or plugging, such as would occur in an actual flue gas. The purpose was to identify purely chemical mechanisms for catalyst poisoning to provide insight into actual deactivation mechanisms. Deactivation studies on actual flue gas slip streams will be conducted as part of a cooperative pilot plant program between EPRI and selected utilities (Flora et al, 1991).

4.4 Catalyst Life

Catalyst "life" is often reported as the number of operating hours between complete replacement of all catalyst in an SCR reactor. In many papers, catalyst life is described as if it is a property of the catalyst. However, it is actually a design variable. For example, there are trade-offs between catalyst life, space velocity, and catalyst replacement

scheduling. In actual installations in Germany and Japan, the catalyst is installed in multiple layers and only one layer is replaced at a time according to a schedule.

In earlier EPRI-sponsored studies (e.g., Bauer and Spendle, 1984), the implicit assumption was that all catalyst would be replaced simultaneously at the end of a specified time interval. This leads to unnecessarily high operating costs. Japanese catalyst vendors and German SCR operators have both reported on the economic benefits of phased catalyst replacement schemes (e.g., Appendix B of Bauer and Spendle, 1984).

In a recent EPRI study, Robie et al (1991) assume that a catalyst life of four years will be realized for U.S. coal-fired high-dust applications. They also assume the same life for tail-end applications even though there are clear differences in operating environments for the two cases. This type of assumption may unnecessarily penalize the tail-end configuration when in fact the major benefit of this configuration is a decrease in catalyst activity loss over time.

4.5 Catalyst Disposal

In Japan and Germany, spent catalyst is returned to the manufacturer. In Japan, catalyst manufacturers have not found it economical to regenerate the catalyst, and the catalyst is often simply disposed of (Lowe et al, 1991). It is likely that spent catalyst would be classified as a hazardous waste in the U.S.

4.6 Impacts on Other Plant Components

SCR has effects on other components of the power plant, particularly for high-dust designs. According to Robie et al (1991), the main impacts are on the boiler, air heater, and induced draft fan. Other components affected are the FGD process, FGD reheat system, waste disposal system, and water treatment system. These impacts are summarized below.

- **Air Preheater.** Air preheater modifications are required due to the deposition of ammonium sulfates and bisulfates. Heat transfer surfaces must be replaced with heavier gauge metal and, in some cases, modified design surfaces. Additional water wash capability is required for air preheater cleaning. High pressure soot blowers are also required at both the hot and cold ends of the air preheater. Air preheater leakage may increase.
- **Boiler.** Loss of thermal efficiency results from air preheater modifications and, at part load operation, from an economizer bypass, which is required to maintain the reaction temperature in the SCR unit.
- **Induced Draft Fan.** In a new plant, a larger ID fan is required to overcome the pressure drop in the SCR reactor and any other incremental pressure drops

associated with downstream effects. This pressure drop may be up to 11 inches of water.

- Forced Draft Fan. The forced draft fan for the combustion inlet air to the air preheater will have a higher mass flowrate due to increased air preheater air leakage.
- Stack. The increase in the SO_3 concentration of the flue gas could result in increased opacity of the flue gas plume if the SO_3 is not removed in the FGD system. Acid condensation would also be a potential source of concern.
- ESP. Because of the lower operating pressure of the ESP due to the pressure drop of the SCR system, higher flue gas temperature, and increased flue gas mass flow due to air preheater leakage and gases introduced for ammonia injection, the ESP will be required to handle a higher volumetric flow rate. In a new plant, therefore, a larger ESP will be required. The ESP may require additional reinforcement due to the lower, and negative, operating pressure. Although the SO_3 content of the flue gas will increase, the beneficial effect of this on ESP performance may be offset by the increase in flue gas temperature. Ammonium salt precipitation in the fly ash could improve agglomeration and reduce reentrainment.
- Ash Disposal/Reuse. Ammonia compounds contained in fly ash material decompose and release ammonia at elevated pH. Even at lower pH, ammonia fixation with alkaline species could result in an ammonia odor problem. Flyash containing ammonia compounds may not be suitable for use in cement manufacturing.
- Water Treatment. Water treatment in addition to typical plant waste water treatment is required to convert nitrogen species in the air preheater wash water to free nitrogen.
- FGD/Reheat. Because of the higher flue gas inlet temperature and mass flow rate, there will be an increase in the water evaporation rate for wet limestone systems. In addition, steam would be required for reheat. The FGD liquor recirculation rate may need to be increased to maintain the same SO_2 removal efficiency. Alternatively, reheat can be accomplished using flue gas duct burners.
- Auxiliary Power Consumption. The net plant output will be decreased by the electricity required to operate SCR process equipment. In addition, during times of soot blowing, the plant efficiency will be decreased slightly due to the use of process steam. Steam is also used for ammonia vaporization, and dilution air for ammonia injection is taken from the discharge of the primary air fans.

The effects of the tail-end SCR system are not as significant as for the high-dust configuration. The tail-end SCR will result in auxiliary power consumption, flue gas pressure drop, water washing of the reheat gas/gas heat exchanger and associated wash water treatment, increased requirement to eliminate mist carryover from the FGD system, and stack effects due to increased SO_3 concentration and higher stack temperatures. In addition, a duct burner may be required. Sootblowers and ash collection hoppers are not required for the SCR system in the tail-end configuration. In the tail-end configurations, separate dedicated dilution air fans are used for ammonia injection (Robie et al, 1991).

For tail-end systems, the leakage rate of the gas-gas heat exchanger used for reheat has been reported to be as high as 7 percent in German facilities. Such leakage allows untreated flue gas to leak into the treated gas prior to stack discharge, thereby effectively bypassing the SCR system.

4.7 SO₂ Oxidation

In the U.S., flue gases have typically higher SO₂ and SO₃ concentrations than experienced in Japan and Germany due to the predominance of high sulfur coals in many regions of the country. The oxidation of SO₂ leads to downstream effects such as ammonium sulfate and bisulfate formation and acid condensations as previously described. Sulfur trioxide and sulfuric acid formed downstream of the SCR can also lead to attack of duct liners. The formation of these condensates and deposits depends critically on the presence of ammonia and sulfur trioxide in the flue gas. However, to minimize this type of problem in U.S. applications may require optimization of catalysts for specific U.S. markets (Lowe et al, 1991).

According to data reported by Bauer and Spendle (1984), SO₂ oxidation is primarily a function of catalyst formulation, space velocity, and operating temperature.

4.8 Ammonia

A portion of the ammonia injected into the SCR system may pass through the reactor unchanged. Ammonia in the flue gas may react chemically or physically with other constituents of the flue gas, including fly ash. This may lead to maintenance and operational problems. Several key concerns are discussed further.

4.8.1 Ammonia Injection

In commercial SCR systems, a critical design issue is the injection of ammonia into the flue gas upstream of the SCR reactor. A key difficulty in ammonia injection is obtaining a uniform mixture of ammonia in the flue gas. Failure to achieve proper ammonia injection and mixing can lead to channeling of ammonia through the SCR system, resulting in high levels of ammonia slip through the SCR reactor and to downstream components in the flue gas path.

Obtaining a uniform distribution of the injected ammonia in the flue gas upstream of the SCR catalyst is often difficult. Flue gas flow modeling and flow straightening devices are often needed to understand and achieve proper flow distribution. Ammonia injection systems typically consist of 30 to 40 injection points per square meter. These injection nozzles are controlled either singly or in groups of several, and the flow of ammonia

through them can be optimized to achieve a reasonably uniform ammonia distribution (± 10 -30 percent) in the flue gas. However, dust deposits on or around the nozzles can lead to plugging of some or alteration of the flue gas flow pattern. Thus, the flow patterns may change over time and require periodic checking and adjustment (Lowe et al, 1991).

4.8.2 Ammonia Retention in Catalyst

Some SCR catalysts may retain ammonia during operation. The ammonia is then released during transients or shut downs. This desorption process may take up to eight hours, based on currently known experience. The ammonia injection rate during low temperature operation should be adjusted to compensate for offgasing of ammonia from the catalyst to maintain ammonia slip within tolerable levels. Because of the absorption/desorption phenomena, changes in NO_x emissions may lag changes in the ammonia injection rate by 30 minutes (Lowe et al, 1991).

Control problems under load swing conditions, exacerbated by the time-lag phenomena, remain an issue, particularly for potential U.S. high sulfur coal applications (Lowe et al, 1991).

4.8.3 Effects on Air Preheater

The most common effect of ammonia slip that is discussed in the literature is the deposition of ammonium sulfates on downstream equipment. However, commercial operation has not always substantiated this concern. For example, in the Takehara Power Station Unit 1, featuring hot-side SCR downstream of a hot side ESP, no additional air preheater washings have been necessary during 34,000 hours of SCR operation. The SCR operates at 80 percent removal efficiency with a NO_x loading of 300 ppm. The lack of plugging of the air preheater by ammonium salts, even inspite of SCR inlet SO_2 concentrations of 1,000 to 1,500 ppm, is attributed to low NH_3 slip levels. These have been 0.2 ppm or less. SO_3 conversion was typically 0.08 to 0.21 percent (Behrens et al, 1991).

The high-dust hot-side SCR system in the Reuter West power station in Berlin, Germany has operated over 15,000 hours on coals with sulfur contents up to 1.2 percent. The typical NO_x removal efficiency is 85 percent with an ammonia slip of 1.5 ppmvd and an SO_2 conversion rate to SO_3 of about 0.5 percent (Behrens et al, 1991). No plugging of the air preheater is reported and no washing of the the air preheater has been necessary since SCR startup. The SCR catalyst layers receive a weekly sootblowing.

In one German power plant, Neckar (1989) reports that approximately 5 percent of the ammonia leaving the SCR system is deposited as an ammonium salt in the air preheater,

with typically about 50 percent of the ammonia absorbed onto fly ash. The ammonium salts are easily soluble in water, and can be washed. As water washing in the air preheater proceeds, the concentration of ammonia in the exiting water stream decreases. Wash water with a high ammonia concentration must be treated to remove the ammonia prior to entering the regular plant wastewater treatment system. Neckar suggests that the initial wash water with a high ammonia concentration can be pretreated separately from the larger volume of water with a low ammonia concentration, which may be suitable for direct feed to the existing waste water treatment plant.

In pilot plant testing of an SCR system, Shiimoto and Muzio (1986) report that ammonia entering the preheater tends to deposit on air preheater surfaces as solid ammonium compounds or to be absorbed onto fly ash. Furthermore, SO_3 in the flue gas is consumed in the formation of ammonium sulfate or bisulfate, and also was absorbed onto fly ash. The investigators report that essentially all of the gaseous SO_3 entering the air preheater during testing was removed from the flue gas.

The effects of deposits include fouling of heat transfer surfaces and increase of pressure drop in flue gas paths. These types of effects may be more pronounced during process upsets (Lowe et al, 1991).

4.8.4 Ammonia Absorption by Flyash

Another concern regarding ammonia slip has emerged in Germany. German experience has been that the typical Japanese criteria of 5 ppm maximum ammonia slip is often not stringent enough to permit commercial use of fly ash as a byproduct. Therefore, in many German installations ammonia slip must be limited to 3 or even 1 ppm (Lowe et al, 1991). Schönbucher (1989) reports that ammonia slip must be limited to 2 ppm to produce a byproduct fly ash acceptable to the cement industry.

Although ammonia does not alter the physical properties of concrete made from fly ash, ammonia captured in the fly ash is released during concrete mixing and may result in a noticeable odor. For ammonia concentrations of less than 60 mg per kg of fly ash, the odor is not noticeable. For the Altback/Deizisau power station Unit 5 in Germany, it appears that 20 to 80 percent of the ammonia slip is captured in the fly ash, with a mean value near 50 percent (Neckar, 1989).

Experimental studies by Shiimoto and Muzio (1986) indicate that most of the ammonia leaving the SCR system exits as a gas, with very little in the form of solid compounds or absorbed by fly ash. However, a portion of the gaseous ammonia is

absorbed by flyash downstream of the SCR reactor, with higher ammonia partial pressures leading to increased absorption.

4.8.5 Ammonia Slip and Tail-End Systems

For tail-end systems, ammonia slip is not a significant concern because of the low concentration of sulfur in the flue gas. Therefore, the constraints on catalyst performance are less severe, allowing potentially greater degradation in catalyst activity (and associated increase in ammonia slip) before replacement is required. Ammonia slip constraints for tail-end systems are typically imposed by air emissions regulations, as opposed to downstream process requirements. Ammonia slip as large as 20 to 30 ppm is not expected to lead to operational problems in tail-end systems. Ammonia odor and plumes become noticeable when the ammonia concentration exceeds 50 ppm (Lowe et al, 1991). Ammonium salt deposition is expected to occur in the gas-gas heat exchanger used for flue gas reheat in tail-end SCR systems. Thus, heat exchanger water washing is also required in this case.

4.9 U.S. Outlook

Because the German and Japanese experiences cannot be directly applied to U.S. applications, EPRI and others are involved in pilot testing of SCR systems on selected slipstreams, analogous to the German testing of over 70 SCR pilot systems. These tests will provide additional data regarding cost and technical feasibility of SCR applied to plants firing domestic medium and high sulfur coals. EPRI will conduct as many as 14 separate tests (Lowe et al, 1991).

In the short term, low-dust tail-end SCR systems hold the most promise of reliable performance for high sulfur coal applications. This type of system would avoid the potentially excessive rate of air preheater fouling and catalyst deactivation that might otherwise be experienced in a high-dust configuration in high sulfur service (Lowe et al, 1991).

There are 105 operating cyclone units in the U.S. totaling over 26,000 MW. These are high NO_x emission technologies which are not easily amenable to combustion NO_x control. The typical NO_x emission rates for these units ranges from 0.8 to 1.8 lb/MMBtu, corresponding to flue gas concentrations of 500 to 1,100 ppm. Many of these units are also located in the midwestern U.S., which is the major source of utility acid rain emissions. Thus, these boilers would appear to be a prime target for application of tail-end SCR systems (Lowe et al, 1991).

5.0 Performance Models

In this section, analytical performance models of SCR systems are presented. These include performance models for high-dust, hot-side and tail-end, low-dust SCR systems. For the hot-side system, downstream effects on the power plant air preheater are modeled. For the tail-end system, a gas-gas heat exchanger and duct burner used for flue gas reheat are modeled.

5.1 Catalyst Requirement

The catalyst requirement is a complex function of the physical and chemical properties of the catalyst, catalyst geometry, catalyst replacement philosophy, reaction temperature, flue gas volumetric flowrate, flue gas characteristics such as NO_x concentration, ash concentration, ash composition, SO_2 concentration, gaseous poisonous species concentration (e.g., As_2O_3), the desired NO_x removal efficiency, allowable flue gas pressure drop, and the desired ammonia slip. The latter in turn affects downstream precipitation of solids, such as ammonium sulfate and bisulfate, and, hence, affects air preheater design in hot-side SCR systems.

Although a catalyst requirement model ideally would be sensitive to all of the above factors, insufficient data are available to support the development of such a model. For example, the interactive poisoning effects of multiple flyash constituents is not well-understood. Therefore, the approach taken here is to develop a model of intermediate detail that captures the key functional dependencies between catalyst requirement and process conditions. The model is based on empirical and design assumptions supplied by the user and power plant performance parameters calculated from the power plant performance model.

A number of theoretical models were reviewed as a possible basis for model development. In most cases, these models were not adopted directly here, but were used to identify key functional dependencies that could be modeled based on empirical data.

5.1.1 Factors Affecting Catalyst Requirement

In a report prepared by Shiimoto and Muzio (1986), there is an appendix containing comments by Kawasaki Heavy Industries, a Japanese manufacturer of SCR systems. KHI presents the development of a simplified equation for estimating catalyst space velocities based on NO_x removal efficiency, ammonia slip, linear velocity, reaction temperature, and catalyst activity. The functional form of this equation is a basis for the performance model developed here.

The simplest model of an SCR system for the purpose of determining catalyst requirement is based on a rate model for the chemical reaction of NO with NH₃, which is the predominate reaction occurring in the SCR reactor. Under the condition of an NH₃/NO_x molar ratio of 1.0, pilot plant testing in Japan has shown that a first order reaction occurs:

$$\frac{d[\text{NO}_x]}{dt} = -k[\text{NO}_x] \quad (15)$$

Integration of this equation yields the following relation between flue gas residence time in the catalyst and NO_x removal efficiency:

$$t = \frac{-\ln(1-\eta_{\text{NO}_x})}{k} \quad (16)$$

The catalyst space velocity is related to flue gas residence time in the catalyst by the following:

$$\text{SV (1/hr)} = \frac{3,600 \text{ sec/hr}}{t \text{ (sec)}} \quad (17)$$

Therefore, the catalyst space velocity is given by:

$$\text{SV} = \frac{3600 k}{-\ln(1-\eta_{\text{NO}_x})} \quad (18)$$

The rate constant, k , corresponds to the so-called catalyst "activity." The catalyst activity is a complex function of catalyst geometry, chemical formulation, and operating conditions.

In the typical case where the NH₃/NO_x molar ratio is less than 1.0, the apparent catalyst activity will be less than the actual catalyst activity. This is because the reaction between NH₃ and NO_x is 1:1, while for molar ratios of less than 1, the active sites populated with ammonia molecules are fewer than the active sites sought by NO_x molecules. This is not a limitation of the catalyst, but rather a limitation due to the scarcity of NH₃.

To adjust for this phenomena, KHI developed an empirical correction factor based on the "end-mole ratio," which is the NH₃/NO_x molar ratio at the SCR reactor exit. The end-mole ratio is the molar ratio of ammonia slip to unreacted NO_x. Thus, Equation (18) becomes:

$$\text{SV} = \frac{3600 C (r_e)^a}{-\ln(1-\eta_{\text{NO}_x})} \quad (19)$$

Figure 7. Regression Model of Space Velocity as a Function of NO_x Removal Efficiency and End-Mole Ratio.

The value of the exponent "a" is obtained empirically from test data obtained for constant conditions except for changes in NO_x removal efficiency and end-mole ratio. Data plotted by KHI suggest that a typical value of "a" is 0.3.

Equation (19) was used as the basis for a regression model for space velocity based on design data provided by KHI in an earlier SCR design study published by EPRI (Bauer and Spendle, 1984). The purpose of the regression model was to determine the adequacy of the simplified model of Equation (19) for use in an SCR performance model. The results are shown graphically in Figure 7.

The regression analysis indicated that Equation (19) was valid for estimating space velocities for NO_x removal efficiencies of 80 and 90 percent, with varying end-mole ratios. However, the model could not also be applied simultaneously to the data for 60 percent NO_x removal. The results here suggest that the catalyst activities differ for the two sets of data. The design details, such as linear velocity, are not reported by Bauer and Spendle (1984); therefore it is possible that design conditions were not the same for the two sets of data. Thus, it appears that the simple model of Equation (19) is a reasonable basis for correcting space velocity for differences in NO_x removal efficiency and end-mole ratio when all other factors are held constant.

To compare catalysts under different operating conditions, KHI suggests the following model:

$$\frac{\ln(1-\eta_2)}{\ln(1-\eta_1)} = C_r H_r \beta_r f_r S_r Q_r \left(\frac{m_2}{m_1}\right)^{0.3} \quad (20)$$

From Equation (20), the performance of a specific catalyst may be estimated based on ratios of key performance parameters, assuming a reference catalyst. This formulation suggests that space velocity can be estimated based on a reference catalyst using multiplicative correction factors to adjust for differences in operating conditions.

Other models are possible, such as that reported by Chen et al (1991). The NO_x removal efficiency is estimated in this model based on detailed design information regarding the SCR catalyst, including catalyst geometry, film mass transfer coefficient, effective diffusivity, and reaction rate constant. However, data to support this detailed model are often not reported in published literature.

5.1.2 Model Form

The modeling approach adopted here is to assume a reference catalyst and to apply a series of multiplicative correction factors to adjust space velocity for different design conditions. The general formulation is:

$$SV = SV_{ref} \prod_{i=1}^4 f_i \quad (21)$$

Each correction factor, f_i , is a ratio that reflects the difference in space velocity from the reference to design conditions due to differences in certain design parameters. If the reference and design conditions are the same, these correction factors have a value of unity. A total of four correction factors have been developed, based on: (1) NO_x removal efficiency; (2) end-mole ratio; (3) catalyst activity; and (4) reaction temperature.

Default reference conditions are included in the model. The reference parameters required include space velocity, NO_x removal efficiency, NO_x inlet concentration, ammonia slip concentration, a catalyst activity curve, a catalyst life, and an operating temperature.

5.1.2.1 NO_x Removal Efficiency

The correction factor for NO_x removal efficiency is based on the model formulation suggested by KHI. This correction factor is:

$$f_1 = f_{eff} = \frac{\ln(1-\eta_{ref})}{\ln(1-\eta)} \quad (22)$$

As the NO_x removal efficiency increases, the catalyst space velocity decreases, leading to a larger catalyst volume.

For tail-end SCR, a portion of the flue gas exiting the FGD system leaks across the gas-gas heat exchanger used for flue gas reheat. Therefore, a portion of the NO_x in the flue gas will also pass across the heat exchanger and into the stack gas. Because of this, the NO_x removal efficiency in the SCR unit must be increased to compensate for the NO_x that bypasses the SCR system due to leakage. The required NO_x removal efficiency for the SCR system is calculated based on the overall NO_x removal efficiency required and the flue gas leakage rate across the gas-gas heat exchanger:

$$\eta = \frac{\eta_{\text{overall}}}{(1 - f_l)} \quad (23)$$

To satisfy this equation, the following constraint must be met:

$$\eta_{\text{overall}} + f_l \leq 1 \quad (24)$$

This model assumes no additional NO_x formation in the duct burner.

5.1.2.2 End-Mole Ratio

The correction factor for end-mole ratio is based on the design ammonia slip, the design inlet NO_x concentration, and the design NO_x removal efficiency. The end-mole ratio is given by:

$$r_e = \frac{[\text{NH}_3]_{\text{out}}}{[\text{NO}_x]_{\text{in}} (1 - \eta)} \quad (25)$$

The correction factor for end-mole ratio is given by:

$$f_2 = f_{r_e} = \left(\frac{r_e}{r_{e,\text{ref}}} \right)^{0.3} \quad (26)$$

5.1.2.3 Catalyst Activity

Experimental and commercial SCR operating data indicate that catalyst activity decreases with time, due to physical and chemical changes to the catalyst as previously discussed. The actual rate of catalyst activity deterioration depends on the operating conditions for the SCR reactor, and is usually not constant with time. Typically, there is an initial period of relative rapid catalyst deactivation, followed by a period of gradual activity change. A typical catalyst activity curve is shown schematically in Figure 8.

Schönbucher (1989) presents several curves for catalyst activity as a function of time for high-dust and tail-end SCR systems. For wet-bottom boilers with high-dust SCR,

Figure 8. A Typical Catalyst Activity Curve.

catalyst activity loss may range from 25 to 45 percent during the first 2,000 hours of operation, with less rapid changes during subsequent operation. For other applications, such as tail-end systems on wet or dry bottom boilers, catalyst activity loss is slight (e.g., 5 percent) over 10,000 hours of operation and appears to decrease at a relatively constant rate.

To model catalyst activity loss, a simple function is employed to represent the catalyst activity curve. The purpose of this function is to provide a reasonable representation of the qualitative properties of catalyst activity loss for most cases. This function features two components: a minimum activity level and an exponential decay from the initial activity to the minimum activity levels. The initial activity is assumed to have a value of unity, while subsequent activity levels are relative to the initial activity.

$$A(t) = A_{\min} + A_{\text{inc}} \left\{ \exp \left(-\frac{t}{\tau_a} \right) \right\} \quad (27)$$

where:

$$A_{\min} + A_{\text{inc}} = 1 \quad (28)$$

A model user specifies the minimum activity level, $A_{\min}$, which determines the incremental initial catalyst activity, A_{inc} , that is subject to exponential decay. By also specifying one data point on the activity curve (an activity level $A(t_1)$ at time t_1), the activity decay time constant, τ_a , can be estimated:

$$\tau_a = - \frac{t_1}{\ln \left(\frac{A(t_1) - A_{\min}}{A_{\text{inc}}} \right)} \quad (29)$$

For example, suppose we have a catalyst with a long term activity level of 75 percent of the initial value, and for which the measured activity after 8,000 hours was 85 percent of the initial activity. Then:

$$A_{\min} = 0.75$$

$$A_{\text{inc}} = 1 - A_{\min} = 0.25$$

$$\tau_a = - \frac{t_1}{\ln\left(\frac{A(t_1) - A_{\min}}{A_{\text{inc}}}\right)} = - \frac{8,000}{\ln\left(\frac{0.85 - 0.75}{0.25}\right)} = 8,730$$

and:

$$A(t) = 0.75 + 0.25 \left\{ \exp\left(-\frac{t}{8,730}\right) \right\}$$

This example is shown graphically in Figure 9. In addition, a case in which the minimum activity level is assumed to be zero is also shown, to illustrate the flexibility of Equation (27) for representing catalyst activity curves.

In typical SCR systems, multiple catalyst layers are employed. Furthermore, these catalyst layers are generally not replaced simultaneously. The overall catalyst relative activity in the case of multiple layers is the average of the individual catalyst layer relative activities (e.g., Nakabayashi and Abe, 1987). If we have N_c identical catalyst layers, and if each layer has been on-line for t_i hours at time t , then the average catalyst relative activity at any time t is given by:

$$A_{\text{avg}}(t) = \frac{1}{N_c} \sum_{i=1}^{N_c} A(t_i) \quad (30)$$

However, we are usually interested in the activity at the design point of the catalyst, which corresponds to the activity level at the end of a catalyst layer replacement cycle. If we have N_c identical catalyst layers that are replaced one-at-a-time every t_r hours, the catalyst relative activity at the design point is:

$$A_{\text{des}} = \frac{1}{N_c} \sum_{i=1}^{N_c} A(i \cdot t_r) \quad (31)$$

Figure 9. An Example Catalyst Activity Curve.

The implications of Equations (30) and (31) are illustrated in Figure 10. In this figure, the instantaneous average catalyst activity of a three-layer catalyst is illustrated for two cases. The first case, shown in a solid line, assumes that one catalyst layer is replaced every 10,000 hours, with a total time between complete catalyst replacements of 30,000 hours. The second case, shown as a dotted line, assumes that all catalyst layers are replaced simultaneously every 20,000 hours. For this particular illustrative case study, the design activity levels of both schemes are approximately the same. However, it is clear that by replacing individual layers sequentially, rather than simultaneously, the effective catalyst "life" is increased for a given volume of catalyst. In the illustrative example, catalyst life is 50 percent greater for the sequential replacement scheme compared to the simultaneous

Figure 10. Illustrative Example of Average Catalyst Activity for a Three Layer Catalyst.

replacement scheme.

In the more general case, sequential replacement schemes may lead to larger initial catalyst volumes in order to achieve the same design activity as a simultaneous replacement scheme. For example, if we simultaneously replace all three catalyst layers in the illustrative problem every 10,000 hours, the design activity level would be approximately 80 percent. To achieve this design activity level with a sequential replacement scheme of one layer every 10,000 hours, the initial catalyst charge would need to be 20 percent larger, which increases capital costs. However, the annual costs associated with catalyst replacement would be reduced by 60 percent, because in the sequential scheme the same amount of catalyst is replaced in 24,000 hours as is required every 10,000 hours in the simultaneous replacement scheme. Thus, selection of a catalyst "life" design value involves trade-offs between capital and annual costs.

Another catalyst charging and replacement scheme involves using an initial charge less than the ultimate design catalyst quantity. For example, three catalyst layers might be used initially, with a fourth layer added at a later time. Then, the four catalyst layers are replaced sequentially similar to the previous case. This example is shown in Figure 11. The example has a design relative activity slightly less than that of the case in Figure 10, which implies that a larger overall catalyst volume is required to achieve the same actual design activity. However, the initial catalyst charge and the periodic catalyst replacement rate are nearly 20 percent less than that for the previous case. This system achieves a better utilization of catalyst. However, a disadvantage of this approach is an increased flue gas pressure drop across the reactor at the design point, due to the requirement for approximately 10 percent additional total catalyst charge compared to the previous case.

For the purpose of estimating a catalyst space velocity based on a reference data point, recall from Equation (18) that space velocity is directly proportional to catalyst activity. Therefore, the correction factor for space velocity due to differences in catalyst activity and catalyst replacement schedules is given by:

$$f_3 = f_A = \frac{A_{des}}{A(t_{ref})} \quad (32)$$

The design activity is calculated using Equation (31) based on the total number of layers to be included in the steady-state catalyst charge (i.e. including layers added to the initial charge at a later time). The reference activity level is estimated assuming that the entire catalyst charge is replaced simultaneously at time t_{ref} .

Figure 11. Illustrative Example of A Catalyst Addition and Replacement Scheme

5.1.2.4 Temperature

A temperature correction is assumed based on the Arrhenius relation for the reaction rate constant, which is given by:

$$k = k_0 \exp\left(\frac{-E_a}{RT}\right) \quad (33)$$

A regression analysis using data from Bauer and Spendle (1984) was done to determine a value for the quantity E_a/R for use in the performance model. This was accomplished by rewriting Equation (19) as:

$$C = k_0 \exp\left(\frac{-E_a}{RT}\right) = \frac{-\ln(1-\eta_{NO_x})(SV)}{3600(r_e)^a} \quad (34)$$

The quantity C was calculated using data presented in graphical form for NO_x removal efficiency as a function of temperature for a given ammonia slip, space velocity, and inlet NO_x concentration. From the regression analysis, the quantity E_a/R was estimated to be 7180, with an R^2 of 0.77 for 18 data points. Thus, the correction factor to adjust space velocity for differences in temperature is given by:

$$f_4 = f_T = \frac{\exp\left(\frac{-7180}{T}\right)}{\exp\left(\frac{-7180}{T_{ref}}\right)} \quad (35)$$

5.1.2.5 Initial and Annual Catalyst Volume Requirement

The SCR catalyst requirement is calculated based on the space velocity and flue gas volumetric flow rate. In cases where there are no later additions of catalyst layers, the catalyst volume is constant throughout the life of the plant. However, some designs

assume that a new catalyst layer is added after some time period. In this case, the space velocity will decrease when the new layer is added. Thus, the total number of active catalyst layers may consist of catalyst layers existing at plant start-up and additional reserve layers added afterwards:

$$N_C = N_I + N_R \quad (36)$$

The initial catalyst volume is given by:

$$V_{c,i} = \frac{G_{FG}(N_I)}{SV(N_C)} \quad (37)$$

The total catalyst volume is similarly given by:

$$V_c = \frac{G_{FG}}{SV} \quad (38)$$

The annual catalyst replacement rate depends in part on the catalyst design. In some studies, it is assumed that all catalyst layers are replaced simultaneously, while others assumed a phased approach to catalyst layer replacement. The number of catalyst layers replaced at the end of each replacement interval is given by:

$$N_{C,r} = 1 \text{ or } N_C \quad (39)$$

If only one layer is replaced at a time, then $N_{C,r}$ equals one. If all layers are replaced simultaneously, it equals the total number of layers in the catalyst. The number of layers replaced per year is:

$$N_{C,a} = \frac{N_{C,r}(8,760 \text{ hr/yr})c_f}{t_r} \quad (40)$$

Thus, the catalyst volume replaced per year is:

$$V_{C,a} = V_C \left(\frac{N_{C,a}}{N_C} \right) \quad (41)$$

The catalyst "life" can be calculated based on the catalyst layer replacement interval and the number of layers replaced at the end of each interval:

$$L_C = \frac{(N_C/N_{C,r})t_r}{(8,760 \text{ hr/yr})c_f} \quad (42)$$

In the case where all catalyst layers are replaced simultaneously, the catalyst life is the same as the catalyst replacement interval. Of course, the total volume of catalyst associated with each replacement scheme will differ.

5.2 Ammonia Requirement

The ammonia requirement is primarily a function of NO_x removal efficiency and the ammonia slip. The ammonia slip depends on the catalyst formulation and space velocity. However, it is treated here as a model input because insufficient data are currently available to develop a model of ammonia slip as a function of other variables. For each mole of NO and NO_2 that reacts in the SCR system, one mole of NH_3 is required (see Equations (3) and (5)). An excess amount of ammonia is required due to limitations related to diffusion of ammonia and NO_x to the catalyst's active sites. Typically, this excess ammonia leaves the SCR system unreacted. Thus, given a specified NO_x removal efficiency and ammonia slip, the molar ratio of ammonia to inlet NO_x is given by:

$$R_A = \eta + \frac{[\text{NH}_3]_{\text{out}}}{[\text{NO}_x]_{\text{in}}} \quad (43)$$

The ammonia mass flow requirement is then given by:

$$M_{\text{NH}_3, \text{in}} = R_A \cdot M_{\text{NO}_x, \text{in}} \quad (44)$$

Ammonia is stored as a liquid. Many design studies assume that the ammonia is vaporized by mixing it with steam prior to injection into the flue gas. A typical minimum ratio of steam to ammonia is approximately 8, based on the use of medium pressure saturated steam. However, for safety reasons, ammonia dilution to 5 volume percent may be required, leading to a requirement for a steam-to-ammonia ratio of 19. The steam requirement for ammonia injection is given by:

$$M_{\text{steam}} = R_S \cdot M_{\text{NH}_3, \text{in}} \quad (45)$$

5.3 SO_3 Oxidation Rate

A portion of the SO_2 in the flue gas entering the SCR reactor is oxidized to SO_3 . The percentage of SO_2 oxidized depends primarily on the reaction temperature, catalyst space velocity, and catalyst formulation. Regression analysis was used to develop two models representative of catalysts formulation for high sulfur and low sulfur operating environments. Data for both of these analyses were obtained from Bauer and Spendle (1984). For the high sulfur catalyst, which would be employed in high-dust hot-side applications, the fraction of SO_2 oxidized to SO_3 , based on 31 data points, is given by:

$$f_{\text{ox}} = 2.38 \times 10^{-13} \cdot S \cdot V^{-1.06} \cdot (T-460)^{5.03} \quad (46)$$

For the low sulfur catalyst, which would be employed in tail-end applications, the fraction is given by the following regression model based on 26 data points:

$$f_{ox} = 1.05 \times 10^{-13} \cdot SV^{-0.996} \cdot (T-460)^{5.05} \quad (47)$$

The coefficient of determination, R^2 , for both of these regression models exceeds 0.99. SO_2 oxidation increases as space velocity decreases and as temperature increases.

5.4 Downstream Effects

Ammonia slip and SO_3 exiting the SCR system can combine to form ammonium sulfate and bisulfate, as previously discussed. Also, ammonia may be captured by fly ash prior to collection in the ESP. These downstream effects are of concern primarily for the hot-side SCR applications.

5.4.1 Air Preheater

The formation of ammonium salts is treated here empirically. Of primary concern is the amount of ammonia associated with ammonium salts deposited in the air preheater. The fraction of ammonia slip that is deposited as ammonium salts in the air preheater is treated as a parameter in the model, rather than as a calculated variable. The fraction of ammonia that is absorbed onto flyash is also a parameter in the model. The remaining portion of the ammonia slip is assumed to exit the plant with the flue gas leaving the stack. The ammonia partitioning coefficients must satisfy the following condition:

$$f_{NH_3,dep} + f_{NH_3,abs} + f_{NH_3,out} = 1 \quad (48)$$

The molar flow rate of ammonia that is deposited as a solid in the air preheater is given by:

$$M_{NH_3,dep} = f_{NH_3,dep} \cdot \frac{[NH_3]_{out}}{[NO_x]_{in}} M_{NO_x,in} \quad (49)$$

Similarly, the molar flows of ammonia absorbed by fly ash and emitted at the stack are given by:

$$M_{NH_3,abs} = f_{NH_3,abs} \cdot \frac{[NH_3]_{out}}{[NO_x]_{in}} M_{NO_x,in} \quad (50)$$

$$M_{NH_3,out} = f_{NH_3,out} \cdot \frac{[NH_3]_{out}}{[NO_x]_{in}} M_{NO_x,in} \quad (51)$$

The ammonia that deposits in the air preheater is removed periodically using water washing. As discussed by Neckar (1989), the concentration of ammonia in the wash water leaving the preheater is initially high, and then gradually decreases. The waste water from

the washing may be separated into high and low ammonia concentration streams, with the high ammonia concentration stream requiring denitrification pretreatment before entering the regular plant waste water treatment system. The model includes provision for specifying the average ammonia concentration of the high concentration fraction of the spent waste water, as well as the portion of the deposited ammonia that is removed by this portion of the water. The model also includes a parameter for the ammonia concentration in the "low concentration" wastewater. These parameters are used to estimate the air preheater wash water requirement, with the concentrations specified in units of mg/l. The "high concentration" wash water requirement, in gallons/hour, is given by:

$$m_{\text{wash,hc}} = \frac{M_{\text{NH}_3,\text{dep}} \cdot f_{\text{hc}}}{4.90141 \times 10^{-7} \cdot C_{\text{NH}_3,\text{hc}}} \quad (52)$$

and the low concentration wash water requirement is given similarly by:

$$m_{\text{wash,lc}} = \frac{M_{\text{NH}_3,\text{dep}} \cdot (1 - f_{\text{hc}})}{4.90141 \times 10^{-7} \cdot C_{\text{NH}_3,\text{lc}}} \quad (53)$$

For tail-end SCR systems, the downstream effects are modeled similarly to those for hot-side systems. The partitioning of ammonia between ammonium salt deposition, ammonia absorbed onto fly ash, and ammonia retained in gaseous form will differ from the hot-side case. However, the gas-gas heat exchanger used for flue gas reheat will be subject to ammonia salt deposition and will require water washing. The spent wash water will require denitrification pretreatment prior to entering the plant waste water treatment system.

5.4.2 Catalyst Sootblowing

Catalyst sootblowing is required to remove ash that may mask or plug the catalyst. A sootblowing design by Bauer and Spendle (1984) is used as a basis to develop a model of the sootblowing steam requirement. The design basis includes steam sootblowing employing multiple sootblower sets. Bauer and Spendle report that the predicted steam requirement is 13,400 lb/hr for a total of approximately one hour per day, or an average of 31 lbmole/hr. There is no indication in the report that the steam requirement is a function of catalyst size, although such a relationship seems plausible. For example, Bauer and Spendle consider catalyst volumes ranging from 10,000 to 30,000 ft³ but apparently assume the same sootblowing steam requirement for all cases. It is assumed here that the steam requirement reported by Bauer and Spendle is typical of the base case catalyst design, which for the high-dust configuration had a catalyst volume of 16,146 ft³.

Furthermore, the steam requirement is assumed to scale with catalyst volume, used here as a measure of catalyst size:

$$M_{\text{soot}} = 31 \left(\frac{\text{SV}}{16,146 \text{ ft}^3} \right) \quad (54)$$

This model does not account for any differences in catalyst masking or fouling rates associated with flue gas or fly ash characteristics.

5.5 Pressure Drop

The flue gas pressure drop associated with the SCR system includes pressure drops across: (1) ductwork and ammonia injection grid; (2) dummy catalyst layers for erosion control; (3) active catalyst layers; and (4) air preheater due to build up of deposits. Each of these sources of pressure drop are treated as input parameters in the model. The total pressure drop, in inches of water, across the SCR system is:

$$\Delta P_{\text{scr}} = n \cdot \Delta P_{\text{cat}} + n_d \cdot \Delta P_{\text{dum}} + \Delta P_{\text{duct}} + \Delta P_{\text{aph, inc}} \quad (55)$$

An additional consideration for hot-side SCR systems is the effect of the reduction in flue gas side pressure on the air leakage through the air preheater. For hot-side SCR systems, a nominal increase in the leakage rate of 10 percent is assumed. This is a model input parameter.

For tail-end systems, which are downstream of the air preheater, there is no incremental pressure drop associated with solids deposition in the air preheater. However, there is a pressure drop associated with flue gas reheating. Therefore, the pressure drop for the gas-gas heat exchanger used for reheat must be included. This pressure drop must be shared between the SCR system and the FGD system, for which reheat is often required also. Thus, a new parameter is introduced which represents the fraction of the gas-gas heat exchanger pressure drop that is solely attributable to the SCR system.

$$\Delta P_{\text{scr}} = n \cdot \Delta P_{\text{cat}} + n_d \cdot \Delta P_{\text{dum}} + \Delta P_{\text{duct}} + \Delta P_{\text{GGH}}(1 - f_{\text{FGD}}) \quad (56)$$

The pressure drop term for ducting includes any pressure drop associated with the duct burner. These values must be specified as model inputs.

5.6 Energy Penalties

The energy penalties for the SCR system include electricity and steam consumption. The largest source of energy use is the incremental electricity required by the induced draft fan to overcome the flue gas pressure drops associated with the SCR system. In addition,

electricity is required for the ammonia injection system, primary to compress vaporized ammonia for injection into the flue gas. Steam is consumed for ammonia vaporization and injection and for sootblowing in the SCR reactor. The steam consumption is converted to an equivalent electricity energy penalty based on the difference in enthalpy between the steam and water at standard conditions, the mass flow of steam used, and the steam cycle heat rate.

The energy penalty associated with operation of the induced draft fan to overcome the SCR flue gas pressure drop is given by:

$$E_{scr,fan} = \left(1.38 \times 10^{-6} \frac{\text{MW}}{\text{cfm} \cdot \text{in H}_2\text{O}} \right) G_{scr,in} \Delta P_{scr} \quad (57)$$

The fan equation here assumes a fan efficiency of 85 percent. This equation also represents the energy penalty associated with a forced draft booster fan used in tail-end SCR systems.

The energy penalty associated with ammonia compression is calculated assuming a 100 psi differential compression with an 85 percent compression efficiency:

$$E_{scr,NH_3} = \left(3.47 \times 10^{-5} \frac{\text{MW}}{\text{lb/hr}} \right) \left(\frac{17.03 \text{ lb}}{\text{lbmole}} \right) M_{NH_3,in} \quad (58)$$

The energy penalty for steam use in the SCR system is calculated based on the steam mass flows, the enthalpy added to the steam by the steam cycle, and the steam cycle heat rate:

$$E_{scr,steam} = \frac{(M_{steam} + M_{soot}) \left(\frac{18 \text{ lb}}{\text{lbmole}} \right) \left(\frac{1,000 \text{ BTU}}{\text{lb}} \right) \left(\frac{\text{MW}}{1,000 \text{ kW}} \right)}{HR_s} \quad (59)$$

The total energy penalty for the high-dust SCR system is:

$$E_{scr} = E_{scr,fan} + E_{scr,NH_3} + E_{scr,steam} \quad (60)$$

For the tail-end SCR system, natural gas used to fire the duct burner represents an additional energy loss. Natural gas is a fuel that could be used to generate electricity. Therefore, the energy penalty is calculated based upon the gross plant heat rate to estimate the equivalent electricity energy penalty associated with natural gas firing:

$$E_{scr,NG} = \frac{m_{NG} HHV_{NG} \left(\frac{\text{MW}}{1,000 \text{ kW}} \right)}{HR_g} \quad (61)$$

The total energy penalty for the tail-end SCR system is:

$$E_{scr} = E_{scr,fan} + E_{scr,NH_3} + E_{scr,steam} + E_{NG} \quad (62)$$

5.7 Flue Gas Reheat for Tail-End SCR

For the tail-end SCR system, the temperature of the flue gas exiting the FGD system must be raised to the reaction temperature required by the SCR system. Furthermore, the temperature of the gas exiting the SCR system can be reduced prior to entering the stack. Therefore, a gas-gas heat exchanger (GGHX) and a duct burner are employed for heating and cooling the flue gas, as shown in Figure 12.

Typically, a Ljungstrum type heat exchanger would be used for the flue gas reheat and cooling system. A portion of the higher pressure flue gas entering from the FGD system will leak into the flue gas stream exiting the heat exchanger to the stack. Therefore, an air leakage stream is modeled. For simplicity, it is assumed that the leakage flue gas is at the FGD system exit temperature. The flue gas leakage mass flow is estimated based on a leakage fraction as follows:

$$M_{\text{leak}} = f_l M_{\text{FGD},o} \quad (63)$$

and the flue gas fraction entering the GGHX is given by:

$$M_{\text{GGH},i} = (1-f_l) M_{\text{FGD},o} \quad (64)$$

In the GGHX, the untreated flue gas is heated from the FGD exit temperature to an intermediate temperature by cooling the treated flue gas exiting the SCR system. The heat transferred across the heat exchanger is given by:

$$Q_{\text{GGH}} = M_{\text{GGH},i} (h_{fg}(T_{\text{inu}}) - h_{fg}(T_{\text{FGD}})) \quad (65)$$

In the SCR computer model, the enthalpy of the flue gas is estimated using regression models for the enthalpy of each flue gas constituent at the given temperature.

The untreated flue gas must be heated an additional amount to reach the SCR reaction temperature. This additional heating is accomplished by use of a duct burner, which also introduces additional mass streams to the flue gas. The mass balance equation is:

$$m_{\text{SCR},i} = m_{\text{DB},i} + m_{\text{NG}} + m_{\text{air}} \quad (66)$$

Assuming that natural gas consists only of methane, the combustion reaction is:

Figure 12. Schematic of Gas-Gas Heat Exchanger Performance Model

For each pound of methane consumed, 3.6 pounds of air are consumed at stoichiometric conditions. If excess air is also considered, the air mass flow is then given by:

$$m_{air} = 3.6(1+r_{ea})m_{NG} \quad (68)$$

The energy balance equation for the duct burner may be written as:

$$m_{SCR,i}h_{fg}(T_{SCR}) = m_{DB,i}h_{fg}(T_{int}) + m_{NG}h_{NG}(T_{NG}) + 3.6(1+r_{ea})m_{NG}h_{air}(T_{air}) + m_{NG}\Delta H_r \quad (69)$$

The heat of reaction for methane is 345,700 BTU/lbmole. In Equation (70), all variables are specified except for the natural gas mass flow rate. Therefore, this equation can be used to solve for the natural gas requirement:

$$m_{NG} = \frac{m_{SCR,i}h_{fg}(T_{SCR}) - m_{DB,i}h_{fg}(T_{int})}{h_{NG}(T_{NG}) + 3.6(1+r_{ea})h_{air}(T_{air}) + \Delta H_r} \quad (70)$$

In the SCR system, ammonia and steam are added to the flue gas, and the flue gas composition changes due to chemical reactions occurring in the reactor vessel. The SCR exit temperature is assumed to be the same as the inlet temperature. The flue gas exiting the SCR unit is cooled in the GGHX. The uncorrected temperature of the treated flue gas exiting the GGHX is estimated from the following relationship:

$$h_{fg}(T_{unc}) = h_{fg}(T_{SCR}) - \frac{Q_{GGH}}{m_{GGH,o}} \quad (71)$$

This equation is solved using an iterative technique to determine the flue gas temperature.

The treated flue gas from the SCR system is mixed with the flue gas leaking across the GGHX prior to entering the stack. The flue gas temperature entering the stack, corrected for the thermal mixing with the leakage air, is estimated using the following equation:

$$h_{fg}(T_{out}) = \frac{m_{GGH,o}h_{fg}(T_{unc}) + m_{leak}h_{fg}(T_{FGD})}{m_{out}} \quad (72)$$

where:

$$m_{out} = m_{GGH,o} + m_{leak} \quad (73)$$

6.0 Model Status and Future Work

The analytical performance model documented here has been implemented into the Integrated Environmental Control Model (IECM) developed by Rubin et al (1986; 1991). Work is underway to complete a revised version of a new cost model for both hot-side and cold-side SCR systems. The new cost model will also be implemented in the IECM, and will be documented in a future report.

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8.0 APPENDIX: NOMENCLATURE

8.1 English Letter Symbols

a	=	Constant
A_c	=	Catalyst area, ft ²
$A_{\min}$	=	Minimum catalyst activity level
A_{inc}	=	Incremental catalyst activity subject to exponential decay ($1-A_{\min}$)
AV	=	Area velocity, ft/hr
c_f	=	Annual plant capacity factor, fraction of year
C	=	Constant representing catalyst activity for a given operating condition (e.g., temperature, inlet NO _x concentration) with NH ₃ /NO _x ratio equal to 1.0
$\vec{C}_i$	=	Vector of concentrations of trace species in stream i, ppmw
$C_{\text{NH}_3, \text{hc}}$	=	Concentration of ammonia in "high concentration" wash water, mg/l
$C_{\text{NH}_3, \text{lc}}$	=	Concentration of ammonia in "low concentration" wash water, mg/l
C_r	=	Ratio of catalyst activities for two catalysts.
E_a	=	Activation energy
E_i	=	Energy penalty for system i, MW
f_{FGD}	=	Fraction of gas-gas heat exchanger pressure drop that is normally associated with FGD flue gas reheat.
f_{hc}	=	Fraction of ammonia deposited on air preheater surfaces removed in high concentration wash water.
f_i	=	Generic correction factor
f_l	=	Fraction of flue gas exiting FGD system that leaks across gas-gas heat exchanger in tail-end SCR system
f_{NH_3}	=	Fraction of ammonia slip partitioned to fate i (e.g., "dep"=deposition on air preheater surfaces, "abs"=absorbed by flyash, "out"=emitted with flue gas)
f_{ox}	=	Fraction of SO ₂ oxidized to SO ₃ in the SCR reactor.
f_r	=	Ratio of correction factors for linear velocity and temperature
G_{FG}	=	Flue gas volumetric flow rate, ft ³ /hr at standard conditions
G_{scr}	=	Flue gas volumetric flow rate in the scr system, ft ³ /min
$h_i(T_j)$	=	Enthalpy of gas i at temperature j, BTU/lbmole
H_r	=	Ratio of catalyst layer heights
HR_g	=	Gross plant heat rate, BTU/kWh
HR_s	=	Steam cycle heat rate, BTU/kWh
k	=	Reaction rate constant. Also interpreted as catalyst "activity."
L_C	=	Catalyst life, years
m	=	End-mole ratio
m_i	=	Mass flow rate of species i, lb/hr
M_i	=	Molar flow rate of species i, lbmole/hr
N_C	=	Number of active catalyst layers
$N_{C, a}$	=	Number of active catalyst layers replaced each year, yr ⁻¹
$N_{C, r}$	=	Number of active catalyst layers replaced at each replacement interval
N_I	=	Number of active catalyst layers installed initially
N_R	=	Number of reserve catalyst layers installed at end of first catalyst replacement interval
n_d	=	Number of dummy catalyst layers
Q_r	=	Ratio of flue gas flow rates
P_i	=	Partition factor within a partition factor matrix for trace species i

$P_{i \rightarrow j}$	=	Partition factor matrix for partitioning of trace species from stream i to stream j.
r_e	=	Exit molar ratio of NH_3 to NO_x at SCR reactor outlet.
r_{ea}	=	Ratio of air to stoichiometric requirement (excess air ratio).
R	=	Universal gas constant
R_A	=	Ratio of ammonia to nitrogen oxides, molar basis
R_g	=	Geometric ratio, ft^2/ft^3
R_S	=	Ratio of steam-to-ammonia, molar basis
S_r	=	Ratio of reactor cross-section areas
SV	=	Catalyst space velocity, 1/hr
SV_{ref}	=	Reference catalyst space velocity, 1/hr
t	=	Time, seconds
t_r	=	Catalyst replacement interval, hours
T	=	Temperature
V_c	=	Total catalyst volume, ft^3
$V_{c,i}$	=	Initially installed catalyst volume, ft^3
$V_{c,a}$	=	Volume of catalyst replaced each year, ft^3/yr
$V_{c,r}$	=	Volume of catalyst replaced at each replacement interval, $\text{ft}^3/\text{interval}$
$[\text{NH}_3]_{out}$	=	Ammonia slip, ppm
$[x]$	=	Concentration of species x, molar basis

8.2 Greek Letter Symbols

β_r	=	Ratio of fractions of reactor plugging
ΔH_r	=	Heat of reaction, BTU/lbmole reactant
ΔP_i	=	Pressure drop for component i
η_{NO_x}	=	NO_x removal efficiency, fraction
τ_a	=	Time constant for catalyst activity decay.

8.3 Subscripts

cat	=	Catalyst
DB	=	Duct burner
duct	=	Ducting
dum	=	Dummy catalyst
FG	=	Flue gas
FGD	=	Flue gas desulfurization
GGH	=	Gas-gas heat exchanger
i	=	in
NG	=	Natural gas
o	=	out
org	=	organics
scr	=	Selective catalytic reduction
stm	=	steam
tr	=	trace species
WW	=	Wash water

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