DEMONSTRATION OF SCR TECHNOLOGY FOR THE CONTROL OF NO_X EMISSIONS FROM HIGH-SULFUR COAL-FIRED UTILITY BOILERS

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ABSTRACT

This paper describes the completed Innovative Clean Coal Technology project which demonstrated selective catalytic reduction (SCR) technology for reduction of flue gas NO_x emissions from a utility boiler burning U.S. high-sulfur coal. The project was sponsored by the U.S. Department of Energy, managed and co-funded by Southern Company Services, Inc. on behalf of the Southern Company, and also co-funded by the Electric Power Research Institute and Ontario Hydro. The project was located at Gulf Power Company's Plant Crist Unit 5 (a 75 MW tangentially fired boiler burning U.S. coals having a sulfur content of 2.5 - 2.9 percent) near Pensacola, Florida. The test program was conducted for approximately two years to evaluate catalyst deactivation and other SCR operational effects. The SCR test facility had nine reactors: three 5000 scfm (equivalent to 2.5 MW) and six 400 scfm (equivalent to 0.2 MW). Eight reactors operated on high-dust flue gas, while the ninth reactor operated on low-dust flue gas. The reactors operated in parallel with commercially available SCR catalysts obtained from suppliers throughout the world. Long-term performance testing began in July 1993 and was completed in July 1995. A brief test facility description and the results of the project are presented in this paper.

PROJECT GOALS

Although SCR is widely applied in Japan and western Europe, numerous technical uncertainties are associated with applying SCR to U.S. coals. These uncertainties include:

1) potential catalyst deactivation due to poisoning by trace metal species present in domestic coals but not present, or present at much lower concentrations, in fuels from other countries;

2) performance of the technology and effects on the balance-of-plant equipment in the presence of high amounts of SO_2 and SO_3 (e.g., plugging of downstream equipment with ammonia-sulfur compounds); and

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

These uncertainties were explored by constructing and operating a series of small-scale SCR reactors to expose various commercially available SCR catalysts to a common flue gas derived from the combustion of high-sulfur U.S. coal. Catalysts evaluated include honeycomb- and plate-type of various commercial compositions from the U.S., Japan, and Europe. First, long-term SCR catalyst performance was evaluated for two years under realistic operating conditions similar to those found in U.S. pulverized-coal-fired utility boilers. Deactivation rates for exposed catalysts were documented to determine life and associated process economics. Second, short-term parametric tests were performed during which SCR operating conditions were adjusted above and below design values to observe catalyst performance. The performance of air preheaters was also observed to evaluate the effects of SCR operating conditions on heat transfer, pressure drop, and boiler efficiency.

SCR TEST FACILITY DESCRIPTION

The SCR demonstration facility was located at Gulf Power Company's Plant Crist in Pensacola, Florida. The facility treated a flue gas slip-stream from Unit 5, a commercially operating 75 MW (nameplate) unit, firing U.S. coals with a sulfur content ranging from 2.5 - 2.9 percent. Unit 5 is a tangentially fired, dry bottom boiler with hot- and cold-side electrostatic precipitators (ESPs) for particulate control. The test facility consisted of nine reactors operating in parallel for comparisons of commercially available SCR catalysts obtained from suppliers throughout the world. With all reactors in operation, the amount of combustion flue gas that could be treated was 17,400 scfm or 12 percent (about 8.7 MW) of Unit 5's capacity. Table 1 shows the average test facility flue gas constituent concentrations measured over the life of the project. Also shown are representative particulate loadings.

Table 1: Test Facility Inlet Flue Gas Composition

Constituent	Average	Data Source
Unit Load (MW)	63	continuous data average over project life
NO_x (ppmv at actual O_2)	314	continuous data average over project life
O_2 (%)	4.8	continuous data average over project life
CO_2 (%)	14.7	continuous data average over project life
SO_2 (ppm)	1570	continuous data average over project life
SO_3 (ppm)	4	average of parametric test data
HCl (ppm)	104	start-up/commissioning test data
NH_3 (ppm)	< 0.4	start-up/commissioning test data
Particulate (gr/dscf)	3.1	estimated by interpolation using average unit load and high/low load start-up/commissioning data

The process flow diagram for the SCR test facility is shown in Figure 1. The facility included three large SCR reactors (5000 scfm, equivalent to 2.5 MW) and six smaller SCR reactors (400 scfm, equivalent to 0.2 MW). Eight of the nine reactors were designed to treat flue gas containing full particulate loading (high dust) extracted from the inlet duct of the hot-side ESP, while one small reactor was designed to treat flue gas extracted from the hot-side ESP outlet (low dust). Only seven of the eight high-dust reactors were operated for long-term and parametric testing.

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

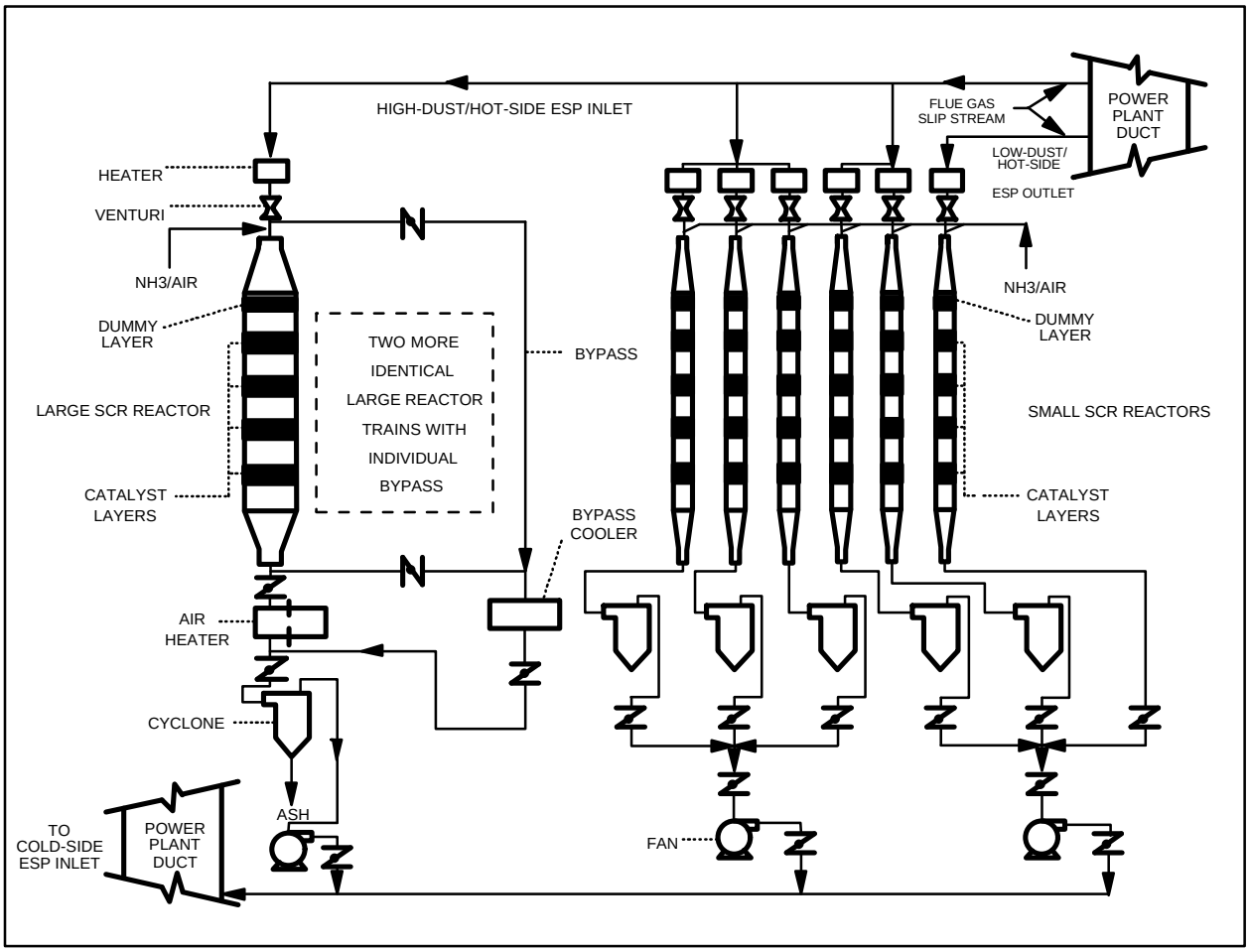


Figure 1. Prototype SCR Demonstration Facility-Process Flow Diagram

For the large reactor trains, the flue gas exited the reactor and entered a specially modified pilot scale air preheater (APH). This modified APH was used to simulate full scale APH's for improved extrapolation of results to commercial scale. The APH's were incorporated in the project to evaluate the effects of the SCR process on APH deposit formation and the effects of the deposits on APH performance and operation.

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

The test facility examined the performance of eight SCR catalysts (one reactor was idled due to the withdrawal of a project participant), each with its own particular geometry, physical design, and chemical make up. Each catalyst supplier was given great latitude in designing their catalyst as long as the following general criteria were met:

- design catalyst baskets to match reactor dimensions
- insure a maximum baseline SO_2 oxidation rate of 0.75 percent
- insure a maximum baseline NH_3 slip at the reactor exit of 5 ppm
- maintain 80 percent NO_x reduction while meeting NH_3 slip requirements
- design for 2-year life while meeting performance criteria
- provide no more than four catalyst layers to meet the design requirements

The characteristics of each catalyst are listed in Table 2. Data include the number of catalyst beds, catalyst type (honeycomb or plate), reactor in which the catalyst was tested, and the total flue gas exposure time.

Coal Supply

One of the primary purposes of this project was to evaluate the performance of SCR technology on U.S. coals. To insure that an adequate database of coal composition was generated, daily as-burned coal samples were acquired from the host boiler. Monthly composites were then used to track both primary and trace coal constituents. Where possible, neutron activation analyses (INAA) were used to augment other measurement techniques.

Average coal analyses for the project are given in Table 3. The analyses include data measured by Alabama Power Company Laboratories (APCo) using atomic absorption and ion-coupled plasma techniques (primary constituents and some trace metals) and data measured by the University of Missouri-Columbia Research Reactor Center using neutron activation analyses (INAA) to supplement trace metals testing. In cases where a constituent was measured by both laboratories, the data give a basis of comparison for the two analytical methods.

Table 2. Catalyst Design Specifications

Parameter	Grace Noxeram	NSKK	Siemens	Grace Synox	Cormetech High-Dust	Haldor Topsoe	Hitachi Zosen	Cormetech Low-dust
Reactor Designation	A	B	C	D	E	F	G	J
Dust Level	High	High	High	High	High	High	High	Low
Composition	V-W/Ti	V-W/ Ti/Si	V/Ti	V/Ti/Si	V-W/Ti	NA[6]	V/Ti	V-W/Ti
Type[e]	HC	HC	Plate	HC	HC	Plate	Plate	HC
Pitch, mm (opening/wall thick.)	7.5 (6.1/1.4)	7.0	5.0	7.5 (6.1/1.4)	7.1 (6.0/1.1)	DNX-16 6.4 hyd.D.	5.5	3.7 (3.2/0.5)
Void Fraction, %	65	70	81	65	71	73	90	72
Density, lb/ft^3	39±3.5	25	37[a]	18±1.5	37	16	23[a]	32
Geom. Surf. Area, m^2/m^3	430	470	383	430	470	455	420	910
Gas Flow, Nm^3/hr	8500	8500	8500	680	680	680	680	680
Gas Flow, scfm	5000	5000	5000	400	400	400	400	400
Catalyst Volume, m^3	3.1	3.026	2.30	0.19	0.245	0.189	0.27	0.097
GHSV @ 0°C, hr^{-1}	2742	2809	3692	3579	2776	3600	2500	7033
Gas Flow Parametric Range (as % of design)	63	91	60	66	60	50	NA	60
Min.	126	127	150	131	150	100	NA	150
Max.								
Cross Sec. Area, m^2 [b]	1.080	1.08	1.106 (1.164)	0.090	0.081	0.094	0.090	0.081
Super.Lin.Veloc.,Nm/§	2.186	2.186	2.135	2.10	2.34	2.00	2.1	2.34
Min.	2.76	2.5	3.203	2.76	3.0	2.5	2.5	3.5
Max.								
Number of Layers	3	3	2	3	3	3	3	2
Temperature, °F	700	700	700	700	700	700	700	700
Temp. Parametric Range, °F								
Min.	660	644	617	660	644	617	626	644
Max.	750	842	806	750	790	752	752	790
% SO_2 Oxidation	0.75	0.5	< 0.6	< 0.75	<0.75	0.68	0.7	< 0.75
Inlet NO_x, ppmv (wet)	400	400	417	400	400	400	400	400
NH_3/NO_x Ratio	0.813	0.811	0.817	0.813	0.81	0.81	0.85	0.81
NH_3/NO_x Parametric Range								
Min.	0.6	0.6	0.6	0.6	0.6	0.6	0.7	0.6
Max.	1.0	1.0	1.2	1.0	1.2	1.2	1.1	1.2
% $deNO_x$	80	80	80	80	80	80	80	80
NH_3 Slip, ppmv (wet)	< 5	5	5	< 5	<5	< 5	< 5	< 5
Particulates, g/Nm^3	6 - 8	6 - 8	6-8	6 - 8	6-8	6-8	6 - 8	NA
Pressure Drop, in. H_2O	3.85 [d]	2.62	1.28	2.60 [d]	2.6	1.73	< 4	3.5
Flue Gas Exposure Time, hr	11012	11859	11632	10151	10151	10175	7293	5363

a. Includes basket, otherwise catalyst density only.
b. Catalyst only. Value in parentheses includes basket.
c. Velocity based on cross-sectional area of catalyst, not basket.
d. For Grace, ΔP includes baskets
e. HC = Honeycomb
f. NA = Not Available

Table 3. Proximate Coal Analysis Data

Test	Analysis Method	Units	APCo data
Moisture, Total	ASTM D 3302	% by Wt.	10.87
Ash	ASTM D 3180	% by Wt.	9.30
Gross Calorific Value	ASTM D 3180	Btu/lb	13268
Sulfur, Total	ASTM D 3180	% by Wt.	2.58
Sulfur	ASTM D 3180	lb/MBtu	1.95
Carbon	ASTM D 3180	% by Wt.	74.82
Hydrogen	ASTM D 3180	% by Wt.	5.00
Nitrogen	ASTM D 3180	% by Wt.	1.58
Oxygen	ASTM D 3180	% by Wt.	6.73
Fixed Carbon	ASTM D 3180	% by Wt.	52.83
Volatile Matter	ASTM D 3180	% by Wt.	37.88

TEST PLAN

The project test plan included five main types of tests:

1) Start-up and Commissioning
2) Long-Term Performance
3) Short-Term Parametric
4) Air Preheater
5) Miscellaneous

Start-up and commissioning tests were performed during the initial start-up of the test facility beginning in early 1993 and continuing until the beginning of long-term operations (July 1993). The remaining types of tests were performed during the two-year period of long-term operations.

Start-Up and Commissioning Tests

The start-up and commissioning of the test facility were of extreme importance to the overall success of the project. Tests were performed to demonstrate that parameters such as ash loading, particle size distribution, flue gas flow, velocity distribution, and flue gas constituents (including trace metals) were comparable between the reactors and were representative of the host unit flue gas parameters. Also, the start-up and commissioning tests showed that the specifications for the test facility design had been met. These basic design criteria are given in Table 4.

Table 4. Test Facility Design Criteria

Parameter	Design Specification
Flue Gas Flow Rate	Control to within ± 2% for large reactors, ± 5% for small reactors
NH_3/NO_x Ratio	Control to within 0.005 of desired NH_3/NO_x ratio
Flue Gas Velocity Distribution	Not more than ± 10% deviation in flow velocity across the cross-section of each individual reactor
NH_3 Distribution	Not more than ± 5% deviation in ammonia distribution
Particulate Concentration	Not more than ± 5% deviation between total mass loading between individual reactors, and not more than ±10 % deviation in particle size distribution

Long-Term Catalyst Performance Testing

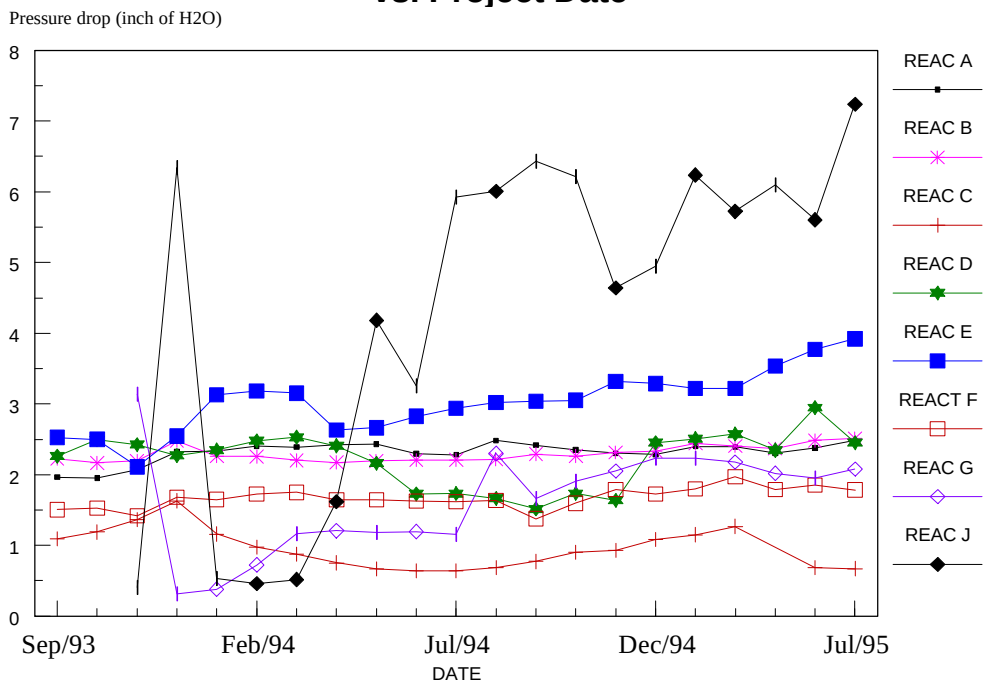
Long-term catalyst testing focused on performance at baseline conditions to evaluate parameters such as catalyst deactivation, ammonia slip, and reactor pressure drop. This evaluation depended on both continuous and periodic measurement of various operational parameters. The reactor baseline conditions under which these long-term tests were performed are identical to the baseline conditions shown for the short-term parametric tests in Table 5.

Catalyst Pressure Drop, Fouling, and Erosion

Reactor pressure drops were measured continuously using the test facility's distributed control/data acquisition system. Figure 2 shows pressure drop across the catalyst beds. The pressure drop created by the dummy beds has been excluded to more closely represent actual catalyst pressure drop. In practice, full scale installations experience very little pressure drop across the flow straightening grid, unlike the test facility which required significantly higher dummy bed pressure drops to meet design specifications. To produce a meaningful plot, the data have been limited to periods of operation at or near baseline conditions. Where no data are shown, either the particular reactor or entire test facility was not in operation.

In general, pressure drop was steady over time for most of the test catalysts. This indicates that sootblower operations were providing the cleaning necessary to prevent long-term fouling of the catalysts. Sootblowing normally was carried out on both catalyst and dummy beds every eight hours. The large reactors utilized a traversing rake steam sootblowing system. Steam was injected at approximately 250 psig at a distance of roughly 2 ft above each of the catalyst layers and the dummy layer. The small reactors were sootblown manually using a compressed air lance.

Figure 2. Catalyst Bed Pressure Drop vs. Project Date



Interestingly, due to the delicate nature of the Hitachi Zosen catalyst, this catalyst was not sootblown. This did not, however, adversely affect this catalyst, as the extremely low facial area of the catalyst prevented fouling to a great degree.

Catalyst fouling and erosion were tracked by monitoring reactor pressure drops and by making periodic visual inspections. In commercial SCRs, which have relatively infrequent visual inspections of the catalyst, the primary indication of catalyst fouling is increased reactor pressure drop. In addition, monitoring of NO_x and/or NH_3 slip distributions at the reactor outlet can give an indication of catalyst fouling. Erosion in commercial reactors is tracked through visual inspection and by periodic sampling of the catalyst at which time erosion can be measured in the laboratory. Severe erosion may also be detected by an analysis of catalyst bed pressure drop.

Since catalyst sampling at the test facility required quarterly shut-down of the reactors, visual inspection of all catalyst beds was made at least on a quarterly basis. In practice, other outages were also used to make visual inspections, resulting in frequent inspections. These inspections usually indicated some fouling near the reactor walls. Problems due to this type of fouling were greatly mitigated on the large reactors by the design of the catalyst baskets. Catalyst suppliers had insured a smooth transition of flow from the reactor cross-section to the catalyst open face cross-section, thus preventing significant fouling due to wall effects. The small reactors exhibited more fouling near the reactor walls primarily due to the small size of these reactors thus exacerbating the wall effects. In any case, all high-dust catalysts demonstrated an ability to handle the dust loadings without significant impacts on performance.

With the low-dust reactor, more fouling was noted. This was not a result of catalyst design, but was the result of poor test facility design. Long duct runs with increased heating requirements and a less than optimum take-off scoop contributed to large particulate material being passed through the low-dust reactor system which was not designed for these conditions. Therefore, fluctuation in this catalyst's pressure drop should not be construed as demonstrating the inapplicability of a low-dust configuration.

The harsh environment in which SCR catalysts in coal-fired applications must operate make high physical strength and durability a necessity. Catalyst erosion can be worsened by areas of high velocity or high particulate loading as well as by erosion from sootblowing operations. Severe erosion in certain areas of particular catalysts is accelerated by the fact that eroded areas become the preferred flow path due to locally reduced pressure drop. This phenomenon seems to be more prevalent with honeycomb catalysts; however, leading edge hardening of the catalyst can help to mitigate facial erosion. In the case of some plate catalysts, such as the Siemens, the catalyst support is steel, thus preventing significant erosion past the face of the catalyst. In the case of the Haldor Topsoe catalyst, a face hardening procedure appeared to enhance this catalyst's ability to withstand facial erosion. Little facial erosion was noted on the Hitachi Zosen catalyst likely due to the extremely small cross-sectional area of exposed catalyst (due to extremely thin plates). The majority of erosion on the honeycomb catalysts appeared to be due to aggressive sootblowing procedures (based on the erosion pattern). One exception was the Grace Synox catalyst. This special-design catalyst represents a significant deviation from other honeycomb catalysts currently

marketed. The bimodal design resulted in a relatively soft material which showed significant erosion during the test program mainly indicated by the thinning of the catalyst walls. Also, some dummy bed material initially used in the test facility was considerably less durable than the catalysts. This material exhibited the phenomenon previously discussed where erosion problems were exacerbated by channeling.

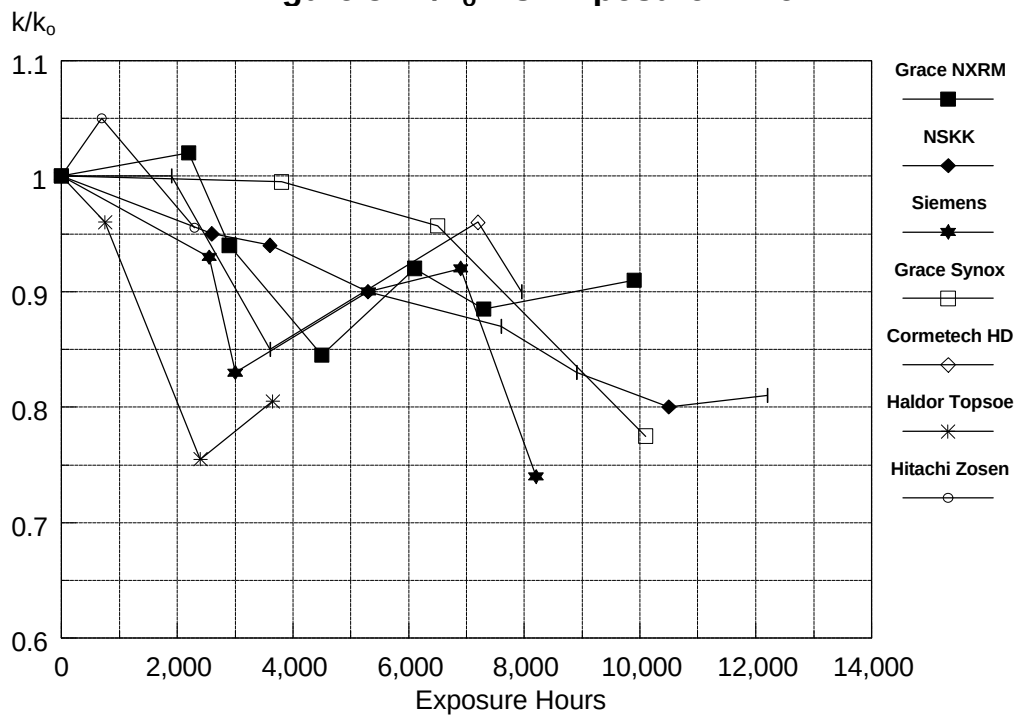
Catalyst deNO$_x$ Activity and Deactivation

As expected, deNO$_x$ varied greatly on an activity per unit bulk volume basis. However, by varying bulk volume, all catalysts met the long-term performance criteria. DeNO$_x$ activity is an important parameter because the bulk volume (and weight) controls to a large degree the number of catalyst beds, physical size, and structure of an SCR reactor and, thus, capital cost. Generally, as NO$_x$ reduction reaches high levels (>90 percent), ammonia slip levels increase dramatically. Further reductions in NO$_x$ and ammonia slip may be achieved by adding additional catalyst. However, capital cost increases substantially, and non-idealities in the reactor design (such as NO$_x$ distribution, ammonia distribution, and velocity distribution) become difficult to overcome.

As previously mentioned, the catalyst suppliers were given a great deal of latitude in specifying the volume of catalyst for their respective reactors. In some cases suppliers chose to minimize catalyst volume by designing a system which met, but did not exceed (improve upon) performance requirements. In other cases, catalyst suppliers chose to increase catalyst volume to achieve improved performance. Honeycomb catalysts are generally considered to have a higher surface area when compared to plate-type catalysts (on a bulk volume basis) and should thus require less volume (although weight may be greater). However, the test program demonstrated that plate-type catalysts can achieve similar results to honeycomb catalysts with equal or less volume. Therefore, overall catalyst volume is affected not only by the basic geometrical (honeycomb/plate) design, but also by the installed catalyst design margin.

One of the purposes of the test program was to address potential catalyst deactivation associated with U.S. high-sulfur coals. Although there was a considerable experience base for foreign coals, little was known about potential catalyst poisons and the resulting catalyst deactivation for U.S. coals prior to this study. Deactivation was tracked through laboratory tests performed by the catalyst suppliers. Catalyst samples were removed from the reactors on roughly a quarterly basis and returned to the respective catalyst supplier for testing. Results were reported directly to SCS. Data are presented in Figure 3. Most aging occurred at a temperature of 700°F, an area velocity of 50 Nm^3/m^2h, an inlet NO$_x$ concentration of 400 ppm, an NH_3/NO_x ratio of 1.0 and an SO_2 concentration of 2000 ppm. These deactivation trends are in keeping with expectations of the catalyst suppliers based on other experience - primarily foreign installations. Trace analyses of potential catalyst poisons such as arsenic and sodium were performed at the individual suppliers' laboratories to correlate these concentrations to the measured deactivation rates. Interestingly, poison levels (especially arsenic) on the catalysts were higher than would be expected for the measured amount of deactivation.

Figure 3. k/k_o^* vs. Exposure Time



*k/k_o is defined as the ratio of catalyst activity at some time to the initial activity of the catalyst

Long-Term Ammonia Slip

The general result of catalyst deactivation is the increase in ammonia slip from the reactor over time assuming $deNO_x$ efficiency is held constant. Catalyst deactivation, however, is not always the source of increases in ammonia slip. Other factors such as maldistributions in NO_x and ammonia, fouling, and erosion can all contribute to increases in ammonia slip over time. As in the test facility, most commercial SCRs operate to achieve a constant $deNO_x$ efficiency in order to meet emission regulations. This practice results in ammonia slip increases as reactor operation becomes less than optimum and the catalyst deactivates. Unfortunately, this ammonia slip is often poorly tracked in commercial SCRs, and thus the overall "health" of the reactor is not known. Consequently, the test facility monitoring program did closely track ammonia slip from the reactors at baseline conditions as well as other parametric conditions to adequately characterize SCR performance.

As expected, ammonia slip increased over the life of the project. Figure 4 shows this general trend using the combination of all test facility catalysts. Data were limited to operation at or very near baseline conditions. It should be noted that the depicted increases in ammonia slip are due not only to catalyst deactivation, but also to degradation in reactor-specific parameters such as NH_3/NO_x distribution, velocity distribution, etc. Careful monitoring of these parameters, however, helped to minimize their contribution to the overall performance degradation of the reactor. The plot shows very low ammonia slip at the start of the project (<2 ppm for all catalysts with an average of less than 1 ppm). As exposure time increased, however, ammonia slip increased, up to an average of roughly 3 ppm, with some catalysts at or near the design limit of 5 ppm.

Figure 4. Intermediate NOx Reduction and Ammonia Slip vs. Time

(base-line conditions)

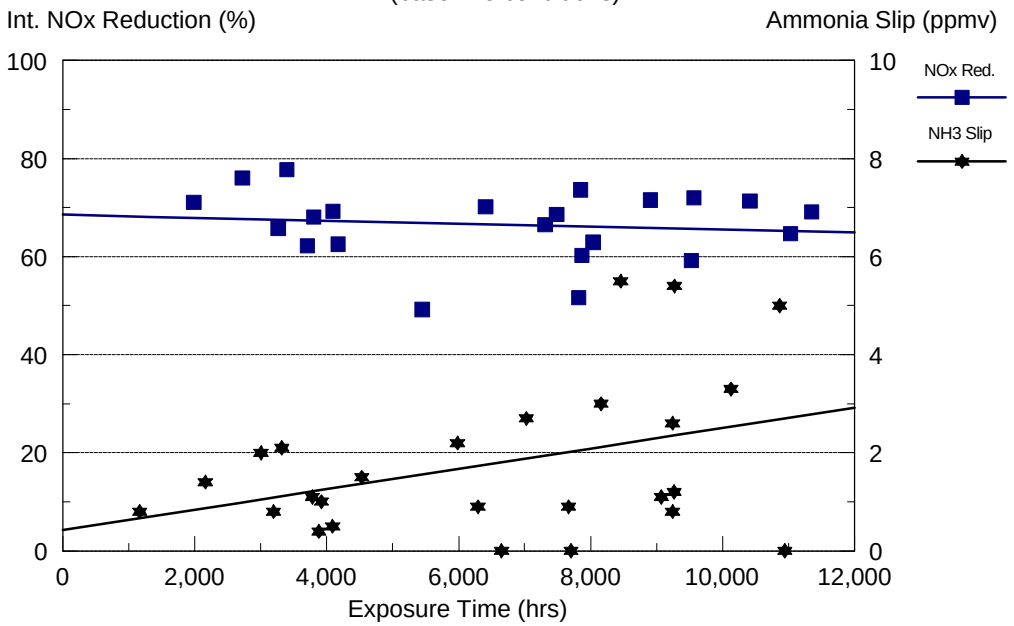
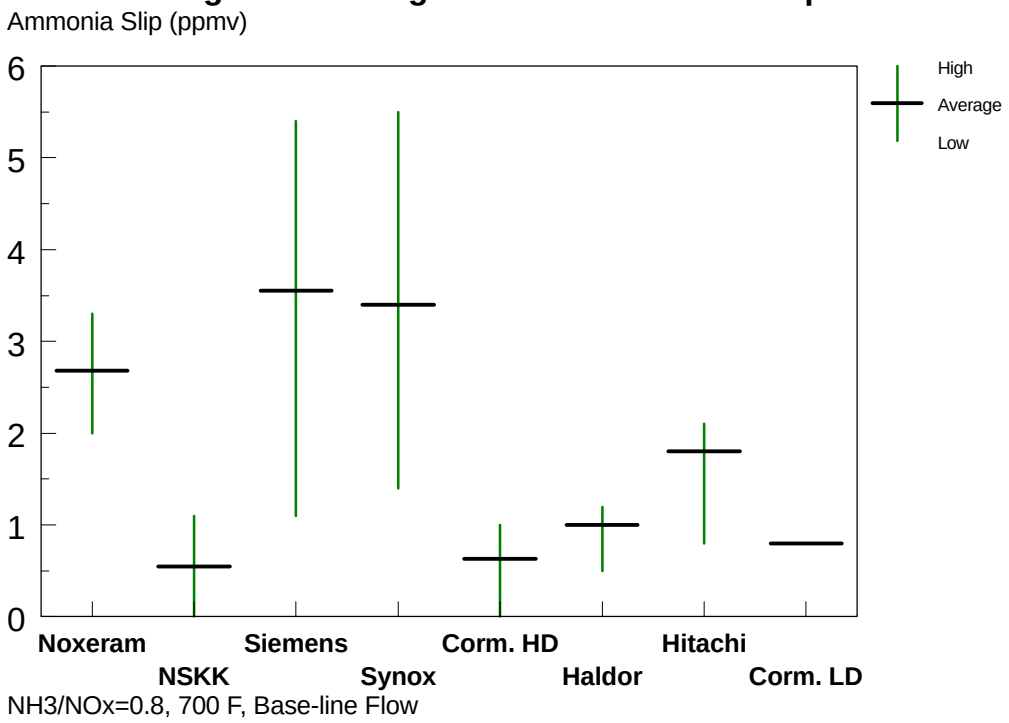


Figure 5 shows average ammonia slip for each of the catalysts on an individual basis using data taken over the life of the project at or near the baseline operating condition. It should be cautioned that ammonia slip is a direct function of catalyst volume, and economics must be addressed in determining the most appropriate catalyst for a particular installation. It should also

Figure 5. Average Base-line Ammonia Slip



be noted that catalyst exposure times differ significantly in some cases (see Table 2). The data presented represent average ammonia slip over the life of the project at conditions very near baseline. High and low values are shown as an indication of measurement variability. The high values shown should not be construed as end-of-project ammonia slip values and therefore do not indicate a failure of the particular catalyst to meet design specifications.

Intermediate NO_x Reduction

Intermediate NO_x reduction was tracked throughout the life of the project using NO_x and ammonia measurements taken upstream and downstream of the first catalyst bed at various conditions during the five parametric test sequences. In general, deactivation based on NO_x measurements is difficult to see in a small scale facility due to the relatively slight decline in activity, especially considering measurement accuracy. However, first bed NO_x reduction measurements are more likely to exhibit catalyst deactivation than over-all NO_x reduction measurement. Because intermediate NO_x reduction is a strong function of the NH_3/NO_x ratio, it can be difficult to discern trends since in practice the actual NH_3/NO_x ratio is difficult to hold constant. However, a large number of points at or near the same NH_3/NO_x ratio can be used to track decreases in catalyst activity. Also shown in Figure 4 is the intermediate NO_x reduction versus catalyst exposure time at baseline conditions. An average value of all reactors has been used to increase the total amount of data available. The plot exhibits a very slight decrease in NO_x reduction over the nearly 12,000 hours of catalyst exposure time. This indicates that on average, the catalysts were not deactivating rapidly as is supported by the laboratory activity tests previously discussed.

Short-Term Parametric Testing

Five sequences of parametric tests were performed on the test facility catalysts during the project life. These tests were designed to examine ammonia slip, deNO_x efficiency (intermediate ammonia), SO_2 oxidation, N_2O formation, NO_x and ammonia distributions, fly ash composition and loading, velocity distributions, and particulate distributions at varying conditions. Table 5 shows the variations in temperature, flow rate, and NH_3/NO_x ratio that were tested. These parametric tests are important in helping to define the operating boundaries of SCR.

Table 5. Parametric Conditions

Parameter	Minimum	Baseline	Maximum
Temperature, (°F)	620	700	750
NH_3/NO_x molar ratio	0.6	0.8	1.0
Space velocity, % of design flow	60	100	150
Flow rate (scfm) -large reactor	3000	5000	7500
-small reactor	240	400	600

Ammonia Slip

In general, ammonia slip, not NO_x reduction, is the controlling factor in the long-term operation of a commercial SCR. Unless extremely severe deactivation has occurred, required NO_x reduction can almost always be achieved if no restriction is placed on ammonia slip. In practice, this is not acceptable due to balance-of-plant impacts and, consequently, limits of ammonia slip

are placed on commercial applications, usually ≤5 ppm. The specifications for the test facility catalysts required baseline ammonia slip not to exceed 5 ppm through the two-year test period.

In addition to ammonia slip depending on catalyst exposure time, it is a strong function of other parameters such as flue gas flow rate, temperature, NH_3/NO_x distribution, and especially NH_3/NO_x ratio. The catalyst design margin partly controls the ability of a particular installation to handle changes in these parameters without exceeding desired ammonia slip levels. In addition, the catalyst design plays a role in its ability to handle parametric changes and consequently some catalysts appear to be more susceptible to increases in ammonia slip due to changes in parametric conditions than do others.

Flow Rate Effects

Theoretically, from a kinetic standpoint, NO_x reduction should be inversely proportional to changes in flow rate. In practice, improvements in mass transfer tend to mitigate some of the effects of increased flow rate and in general flows could be increased to 150 percent of design without the catalyst exceeding the 5 ppm limit at 80 percent NO_x reduction and design temperature. This ability depends on installed margin and design, although sensitivity to this parameter is not excessive.

Temperature Effects

Temperature increases would be expected to significantly improve reactivity. However, in practice, mass transfer limitations become controlling in commercial SCRs, and in the test facility, increases in catalyst activity were not very significant above 700°F. Most catalysts exhibited fairly significant improvements in overall performance as temperatures were increased from 620°F to 700°F, but relatively little improvement was noted as the temperature was increased from 700°F to 750°F. This shows that the benefits of high temperature operation probably do not outweigh the heat rate penalties involved in operating the SCR at the higher temperature.

NH_3/NO_x Ratio Effects

Changes in the NH_3/NO_x ratio and consequently NO_x reduction generally produce the most significant changes in ammonia slip. Decreases in NO_x reduction below 80 percent, down to values of roughly 60 percent, were examined in the test facility. In most cases the ammonia slip at the low NO_x reduction was at or near the ammonia slip detection limit of 1 ppm. As NO_x reduction was increased above 80 percent, ammonia slip also increased. Slip values were fairly reasonable up to NO_x reduction levels of approximately 90 percent. As NO_x reduction increased past 90 percent, however, ammonia slip levels increased dramatically.

SO_2 Oxidation

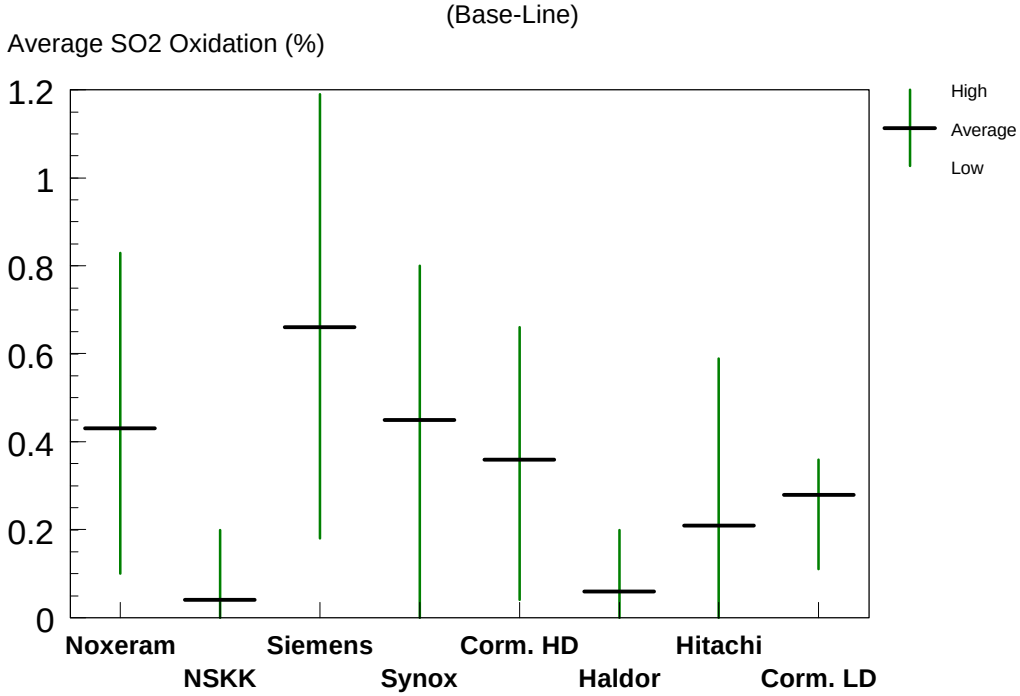
Unfortunately, the catalytically active species that result in deNO_x activity often contribute to SO_2 oxidation activity. Since increased SO_3 is detrimental to downstream equipment, it is essential to operate the SCR reactor at a temperature high enough to achieve the desired level of deNO_x but not high enough to oxidize excessive SO_2. In general, as requirements to minimize SO_2 oxidation relax, deNO_x activity per volume of catalyst can be increased. The upper bound for SO_2 oxidation for the test facility catalysts was set at 0.75 percent at baseline conditions. The oxidation of SO_2

was measured in the test facility at various operating conditions in addition to the baseline measurements. Average SO_2 oxidation rates are shown in Figure 6. These data reflect baseline conditions over the life of the project. All of the catalysts were within the design limits, with most exhibiting oxidation rates well below the specified limit. One notable exception is the Siemens catalyst which had an SO_2 oxidation rate very close to the design value.

In practice, some benefits may be realized by decreasing SO_2 oxidation past some arbitrarily chosen point, but these decreases are generally made at the expense of increasing catalyst volume. As with deNO_x activity, the SO_2 oxidation margin chosen by the individual catalyst suppliers likely contributed significantly to the overall catalyst volume. It is difficult to determine the point of diminishing return for decreasing SO_2 oxidation, as little full-scale long-term operational data are available for U.S. boilers. Although differences in SO_2 oxidation characteristics were very apparent between the catalyst suppliers, these differences do not necessarily denote a difference in catalyst design expertise between the suppliers, but more likely reflect a philosophical decision as to the catalyst offering made. In practice, all suppliers would likely be able to meet application specific SO_2 oxidation requirements (assuming flue gas constituents do not contribute to the oxidation characteristics). Unlike ammonia slip (or catalyst deNO_x activity), the SO_2 oxidation rate of a catalyst is not expected to change significantly with time. This was the general finding based on measurements at the test facility as well as with the catalyst supplier laboratory tests. Since SO_2 oxidation remains relatively constant over time for a given catalyst volume, balance-of-plant effects must be evaluated in terms of the maximum SO_2 oxidation that may occur in later years with the addition of catalyst layers.

Figure 6. Average SO2 Oxidation Rate

(Base-Line)



NH3/NOx=0.8, 700 F, Design Flow

Flow Rate Effects

Due to the reaction order and the relatively constant SO_2 concentration, SO_2 oxidation should be inversely proportional to reactor flow rate (i.e. space velocity, linear velocity). However, most of the test facility catalysts exhibited a fairly constant SO_2 oxidation rate with respect to flow. The Siemens catalyst, with a somewhat higher SO_2 oxidation rate, did exhibit a more linear response to flow rate. It is believed that physical phenomena in the test facility such as SO_3 deposition within the reactor may have masked some of the effects on SO_2 oxidation from flow rate changes.

Temperature Effects

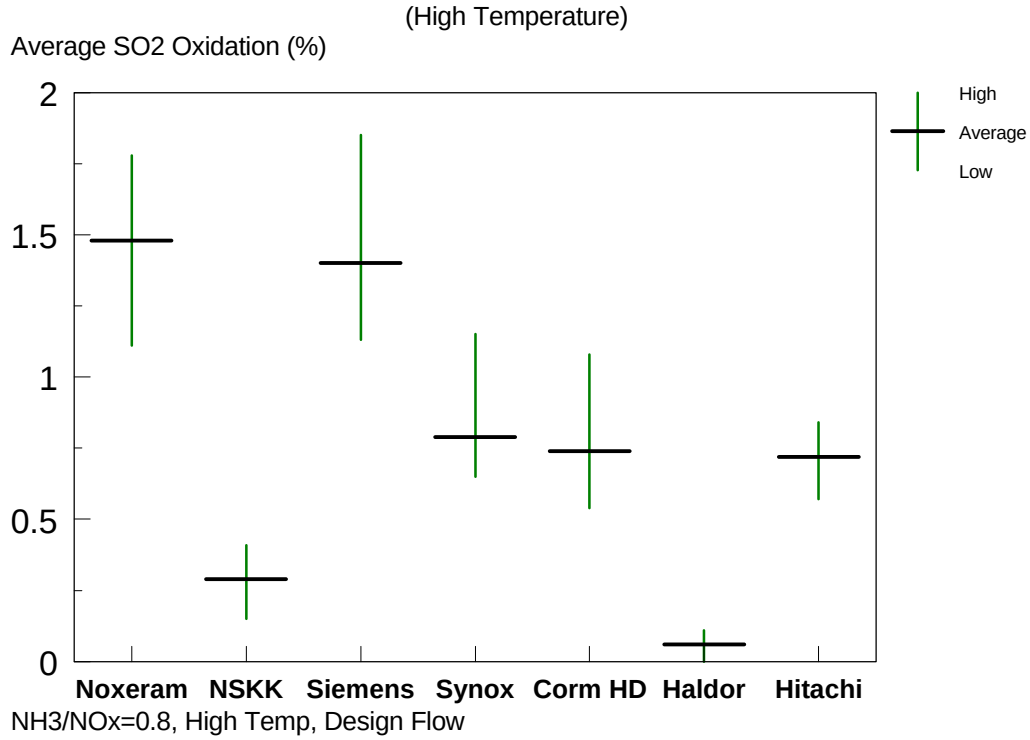
The oxidation of SO_2 is normally a much stronger function of temperature than of flow rate. Theoretically the catalysts should exhibit an exponential relationship of SO_2 oxidation to temperature. However, the measurements in the test facility showed that this relationship was more linear than exponential. Little difference was noted in SO_2 oxidation between 620 and 700 ^{o}F. However, SO_2 oxidation did increase more significantly between 700 and 750 ^{o}F. Figure 7 shows average SO_2 oxidation for the test facility catalysts at high temperature, with fairly significant increases in oxidation rate over baseline values previously shown.

NH_3/NO_x Ratio Effects

The rate of SO_2 oxidation is not expected to be a direct function of the NH_3/NO_x ratio, since ammonia does not play a direct role in the SO_2 oxidation reaction. However, other extraneous factors can create apparent changes in SO_2 oxidation rate with changes in NH_3/NO_x ratio. This is mainly due to physical effects such as precipitation of ammonium bisulfate. Increases in the

Figure 7. Average SO2 Oxidation Rate

(High Temperature)



NH_3/NO_x ratio change the ammonium bisulfate formation patterns between the measurement points and can result in an apparent change in SO_2 oxidation rate. For this reason, most SO_2 oxidation tests were made at 80 percent NO_x reduction.

CONCLUSIONS

SCR Catalysts

All of the catalysts in the test program proved to be acceptable and met design specifications. Significant differences, however, were noted in catalyst parameters such as volume, weight, activity (both $deNO_x$ and SO_2 oxidation), fouling, and pressure drop. As a result, no one catalyst can be considered superior since each may possess advantages particular to the characteristics of a proposed installation. For instance, pressure drop may not be a critical factor in a new-plant installation, but may be critical in the catalyst selection for a retrofit situation where a fan retrofit lies in the balance. Similarly, weight may be the controlling factor for an in-duct installation, while other installations may be particularly concerned with SO_2 oxidation. In short, careful examination of catalyst characteristics is necessary to choose the optimum catalyst for a particular installation.

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