

SCR AND HYBRID SYSTEMS FOR UTILITY BOILERS: A REVIEW OF CURRENT
EPRI-SPONSORED RESULTS

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Keywords: Selective Catalytic Reduction (SCR), NO_x Reduction, Hybrid Systems

Selective Catalytic Reduction (SCR) has been widely demonstrated in Europe and Japan as a postcombustion NO_x control technology. However, most of this experience has been gained using relatively low-sulfur fuels, typically less than 1.5 percent. By comparison, the application of SCR in the United States has been much more limited, and to date the experience base is virtually non-existent for coal- and oil-fired boilers.

Higher fuel sulfur content corresponds to higher concentrations of SO₂ and SO₃ which can lead to potential poisoning and more rapid deactivation of the catalyst. In addition, SCR catalysts have the potential to oxidize SO₂ to SO₃, which can lead to serious problems with ammonium sulfate and/or bisulfate deposition in the air preheater, marketability of fly ash, and potential increases in plume opacity. A number of elements present in fly ash, such as arsenic and alkaline metals, may poison the active sites of an SCR catalyst.

Regulatory forces stemming from the 1990 Clean Air Act Amendments have the potential to require the use of SCR in the U.S. for both new and existing units. In response to uncertainties in the cost and feasibility of SCR for the U.S. utility industry, EPRI has sponsored a multi-pilot plant test program to evaluate the feasibility and cost of SCR as a function of fuel type and SCR/host boiler configuration. This paper discusses three of those pilots: the high sulfur/high dust unit at the National Center for Emissions Research, TVA; the post-FGD unit at EPRI's Environmental Control Technology Center, NYSEG; and the residual oil-fired unit at the NiMo Oswego Steam Station. Each pilot represents a 1 MW(e) equivalent SCR reactor divided into two parallel sections to allow for simultaneous testing of two catalyst types. Operating conditions for each pilot are listed in Table 1.

The pilot SCR catalysts were designed to maintain certain performance criteria over guaranteed and design lifetimes of 2 and 4 years, respectively. Performance goals call for 80% NO_x conversion with residual ammonia (slip) levels of less than 5 and 2 ppm at the exits of the second-to-bottom and bottom catalyst layers, respectively. At TVA (5 catalyst layers), the 5 and 2 ppm slip limits apply to the outlets of the fourth and fifth catalyst beds, and at NYSEG and NiMo (3 layers), the limits apply to the outlets of the second and third catalyst beds.

TVA HOT SIDE, HIGH SULFUR/HIGH DUST SCR PILOT

The TVA pilot was eventually equipped with features to counter the effects of fly ash on the SCR catalysts, including relatively large cell openings, a non-catalytic "dummy" catalyst layer, screens above each catalyst layer, streamlined reactor and sootblowers above the first and fourth layers. The TVA pilot was operated between May 1990 and May 1994 for a total of approximately 22,000 hours.

Catalyst Activity. Both initial TVA test catalysts exhibited significant deactivation which was exacerbated by frequent boiler/pilot shutdowns early in the test program. Analysis of ash samples from the reactor identified a mechanism in which the ash deposits become enriched with sulfur via interaction with ambient moisture during shutdowns. As the moist acidic deposits reacted with alkaline ash constituents, hard deposits were formed that permanently plugged a number of catalyst channels. This mechanism may have also occurred on a smaller scale on the catalyst surface and within catalyst pores, and contributed to formation of a masking layer and consequential loss of catalyst activity.

The original V/Ti catalyst was tested for the entire pilot operating duration. Results of catalyst sample activity measurements by the manufacturer are shown in Figure 1. The measurements were made on small sections of the catalyst sample that were free of plugged channels; therefore, results were directly comparable with data shown in the

figure from selected European experience. In all cases, the samples from bed 1 exhibited a higher activity than those from bed 3, which may indicate the positive influence of sootblowers located above the first catalyst layer, but not above the third layer.

Figure 1 also shows the activity curve for replacement V/Ti test elements installed in the center of catalyst beds 1 and 3 for approximately 8,000 hours exposure. The replacement elements featured different hardness values than the original catalyst charge. Although the replacement elements exhibited a lesser rate of deactivation, the positive effects of altering catalyst hardness are not entirely conclusive because a lower sulfur coal was being fired while the replacement elements were in place.

The original zeolite catalyst failed to meet its performance criteria after 5,000 hours of operation and was replaced after approximately 12,000 hours with a reformulated zeolite design from the same vendor. The reformulated catalyst showed improvement in its baseline activity and in the rate of deactivation compared to the original catalyst.

Bulk and surface chemical measurements were also made by both catalyst vendors to monitor changes in the composition of the catalyst and the accumulation of potential catalyst poisons. Bulk analysis results indicate increases in the concentrations of arsenic, sodium, and potassium with increasing exposure time.

Catalyst Plugging Countermeasures. The TVA pilot represented a severe environment with respect to potential catalyst plugging due to the high ash loading and the alkalinity of the ash. Periodic reactor inspections revealed considerable buildup of solids on the outer catalyst blocks, which resulted from "wall effects" in the relatively small reactor. Over the course of the test program, the flue gas pressure loss across the V/Ti catalyst increased from below 4 inches to over 10 inches of water. Manual counting of the plugged channels showed that nearly 55% of all V/Ti catalyst channels had become permanently plugged when testing ended.

A number of strategies were implemented or considered during the test program to limit increases in catalyst channel plugging. These include screens, sootblowers, vacuuming, and moisture avoidance. All strategies employed at the pilot were successful to a certain degree, but their need and practicality for full-scale SCR application will vary.

Other Operating Issues. Several operational issues were encountered during the TVA test program that provided pilot experience with full-scale SCR design implications. These include: ammonia injection nozzle pluggage in the high sulfur/high dust environment; artifact reactions over sampling probe materials during NO_x and ammonia sampling; process control issues associated with zeolite catalyst ammonia adsorption/desorption times, and CEM system maintenance and sample preconditioning issues specific to high sulfur/high dust SCR systems.

NYSEG POST-FGD SCR PILOT

The NYSEG SCR Pilot began testing in December 1991 and is currently operating, with test catalysts exposed to flue gas for approximately 21,000 hours. Key pilot results include catalyst performance in the relatively clean post-FGD environment and cost issues associated with flue gas reheat. A recuperative heat-pipe heat exchanger (HPHE) recovers heat from the gas exiting the reactor and an additional 185°F of reheat input is required to maintain a reactor temperature of 650°F.

Heat Exchanger Fouling Effects. Because the cold end of the NYSEG HPHE operates below the maximum condensation temperatures of ammonium sulfate/bisulfate and sulfuric acid, the test program was focused on evaluating exchanger fouling effects (i.e., heat transfer loss, increase in gas pressure drop, and corrosion).

Figure 2 shows the relative decline in heat transfer and increase in flue gas pressure drop across the return side of the heat exchanger during operating periods with distinct ammonia slip levels. In the figure, heat transfer is expressed as a fraction of the design rate to normalize exchanger efficiency for changes in gas flow and reactor temperature. The figure also shows the effects of internal water-washing between operating periods. Water-washing was very effective in dissolving and removing deposits, and

consequently in restoring heat exchanger performance and pressure drop to original conditions.

Figure 2 also illustrates the importance of minimizing ammonia slip from SCR catalysts in the post-FGD configuration. At the pilot unit, severe heat exchanger performance degradation was avoided when the average ammonia slip was held to below 2-3 ppm.

An extensive corrosion testing program was undertaken to examine the potential problem of cold-end corrosion of the HPHE tubes. The surface temperature of these tubes is typically 60°F colder than the bulk flue gas temperature. The program included on-line corrosion monitoring, test samples, and test heat pipes of various metals. The results of this program are beyond the scope of this paper.

Catalyst Activity. A post-FGD configuration requires less catalyst and problems associated with high flue gas sulfur and fly ash content are avoided. No screens, "dummy" catalyst layers, or reactor sootblowers are required. The overall catalyst volume is lower than its high dust counterpart because of the higher surface area-to-volume ratio inherent to a smaller pitch catalyst. The favorable reactor environment also lessens the rate of catalyst deactivation, and further reduces catalyst volume requirements to achieve a given catalyst life.

The original composite V/Ti catalyst exhibited severe deactivation and was replaced after only 5,300 operating hours. Activity changes occurred exclusively during pilot shutdowns, which suggested that ambient moisture had aided in the mobilization and penetration of catalyst poisons throughout the active catalyst surface layer. Contaminants that penetrated the catalyst included silicon, sodium, potassium, phosphorus, and sulfur, while calcium and iron were concentrated at the surface. The source of the contaminants is the fine ash and FGD carryover solids that are lightly deposited on the catalyst surfaces during operation. The original extruded V/Ti catalyst and the replacement composite V/Ti catalyst showed no measurable activity change in pilot tests over 13,100 and 12,700 hours, respectively. Therefore, given the same performance goals, a post-FGD catalyst would be expected to exhibit a substantially longer catalyst life than its high sulfur, high dust counterpart.

A short testing period was dedicated to catalyst evaluation at temperatures below the typical lower limit of 600°F to determine the potential for reducing the operating temperature in the post-FGD configuration. To accomplish this, SCR catalysts would need to overcome performance effects from kinetic limitations at low temperature, and from possible fouling due to condensation of ammonium-sulfur compounds on the catalyst surface and within the catalyst pores.

At reactor temperature of 550°F, the extruded V/Ti catalyst exhibited marginally lower, but steady performance over 1,400 operating hours even though catalyst fouling was detected. The composite catalyst exhibited a more severe performance decline that varied with changes in the inlet NO_x concentration from the host boiler. After each test period, both catalyst's performance was restored to original levels when the temperature was raised to baseline (650°F) conditions.

NiMo RESIDUAL OIL SCR PILOT

The NiMo pilot unit was operated between October 1991 and October 1993, with flue gas flowing through the unit for approximately 4,800 hours. The host boiler is used for load following, typically cycling down to 20% MCR overnight, and with hourly load changes of up to 60% MCR.

Catalyst Activity. Activity changes were measured by both catalyst vendors on samples taken after 2,400 and 4,100 operating hours. The relative activity of the corrugated plate catalyst increased during both test intervals, and exceeded the original activity by 24% by the end of the test program. The effect was attributed to deposition of vanadium from the flue gas on the catalyst surface, since SO₂ oxidation rates also increased with time over both catalysts. The measured fuel oil vanadium content varied between 55 and 170 ppm during the test program.

The activity of the top layer of composite V/Ti catalyst decreased somewhat during the test program, but no overall performance change was detected via pilot NO_x conversion

and ammonia slip measurements at the reactor exit (after 3 layers). After 4,100 hours, the activity of the top layer declined by roughly 20% based on the average of values from samples taken from the tops of the first and second layers, and essentially no activity change was seen in the second and third beds during the course of the test program.

Deactivation in the first layer was attributed to masking by a thin layer of solids found on the catalyst surface. The catalyst vendor concluded that solids deposition and consequential activity loss at the top of the reactor was exacerbated by the aggressive catalyst pitch (3.6 mm). A more conservative catalyst design and additional measures to prevent solids deposition (i.e., sootblowers above every catalyst level) are advisable for full-scale SCR systems in similar heavy oil service.

Catalyst Plugging and Deposition. Although the particulate content of the flue gas from the NiMo host boiler is considerably less than that at TVA, problems with catalyst deposition and pluggage were encountered throughout the test program. Reactor deposits were found to consist of oil ash, magnesium oxide (MgO) and magnesium sulfate, the magnesium source being fuel oil additives. Plugging countermeasures for the pilot were limited to sootblowers above the first catalyst layer and routine catalyst cleaning during system shutdowns.

Although not proven at the pilot scale, more strict control of MgO usage may reduce solids deposition and catalyst pluggage effects in full-scale SCR systems for residual oil boilers. In addition, sootblowers were found to be highly effective in preventing catalyst pluggage in this service in a detailed evaluation at another EPRI-sponsored pilot.

Other Operating Issues. Operational lessons from the NiMo pilot study include the demonstration of direct liquid ammonia injection, and process control issues associated with inconsistent aqueous ammonia concentrations and deep cycling of the host boiler.

SCR Design and Operational Recommendations Report

Results from all EPRI-sponsored pilots are currently being incorporated into a guidance document entitled *SCR Design and Operational Recommendations: R&D Lessons Learned* (EPRI Report TR-105103). The report will be released later in 1995, and will include results and design implications from the three pilot studies described in this paper, in addition to the results from the advanced SCR pilot system at the Pacific Gas & Electric Company's Morro Bay Station, and the multi-pilot SCR system at Southern Company Service's Plant Crist sponsored under the DOE's Clean Coal Technology Program.

HYBRID SCR

Hybrid selective catalytic reduction (SCR) systems consist of either a combination of SCR techniques (i.e., in-duct SCR combined with air heater SCR) or selective non-catalytic reduction (SNCR) in combination with SCR.

Depending on unit-specific parameters, a hybrid can offer advantages that include: reduced capital cost, higher NO_x reduction without extensive unit modifications; lower system pressure drop; safer and less expensive chemical storage; lower ammonia slip; and operational flexibility. However, a hybrid system can present some drawbacks that may make them less beneficial. These include: system complexity, higher chemical costs, and potentially higher capital costs.

EPRI commissioned a study to document the current experience and develop a tool by which utilities can determine the applicability of Hybrid SCR to meet their NO_x reduction goals, a guideline for selecting the best configuration, and a reference for developing the design parameters necessary to implement the technology. There are a number of technical and commercial considerations which must be resolved prior to designing or procuring a Hybrid SCR system. The boiler operating, temperature, and emissions data necessary for the final design are presented along with the process design variables which must be specified. Procurement suggestions are included to assist the user in addressing some of the more pertinent commercial issues.

Table 1
Typical SCR Pilot Operating Characteristics

	TVA Shawnee Station	NYSEG Kintigh Station	NiMo Oswego Station
Host Boiler Fuel Type	High (2.5-5.0%) S Coal	Med. (1.5-2.5%) S Coal	1.5% S Residual Oil
Pilot Configuration	Hot Side/High Dust	Post FGD	Hot Side
Total Flue Gas Flow, scfm	2100	2000	2000
Reactor Temperature, °F	700	650	700
Inlet NO _x , ppm	450	300	200-1000
Inlet SO ₂ , ppm	2000	150	800
Inlet SO ₃ , ppm	20	5	23
Particulate, gr/dscf	3.0	0.0012	0.091

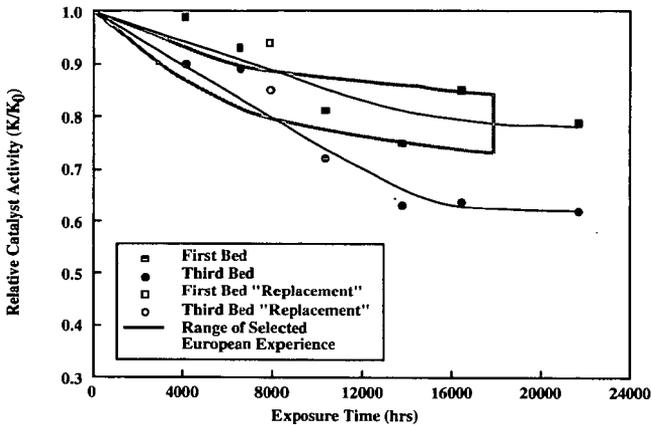


Figure 1
Relative Changes in TVA V/Ti Catalyst Activity vs. Exposure Time

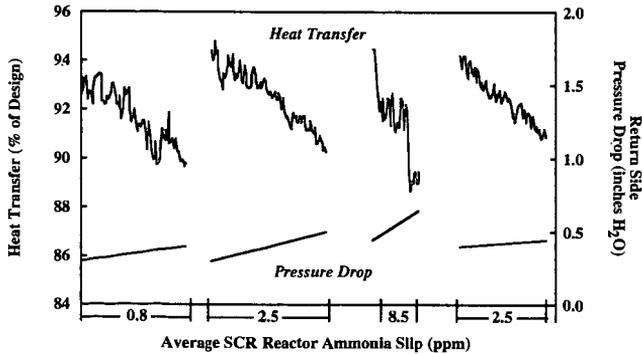


Figure 2
NYSEG Pilot Heat Exchanger Performance and Return Side Pressure Drop vs. Time (Heat Exchanger Was Water-Washed Between Operating Periods)