INDUSTRIAL BOILER RETROFIT FOR NO_X CONTROL: COMBINED SELECTIVE NONCATALYTIC REDUCTION AND SELECTIVE CATALYTIC REDUCTION

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Abstract

A 590 kW (2 MMBtu/hr), oil-fired, three-pass, fire-tube package boiler was retrofit with a combined selective noncatalytic reduction (SNCR) and selective catalytic reduction (SCR) system and demonstrated 85% nitrogen oxide (NO_X) reduction with less than 6 ppm ammonia slip. A urea-based SNCR solution was injected in the first pass, reducing NO_x and providing ammonia reagent for the SCR. A catalyst housing was designed to fit between the second and third passes, where the access doors of the boiler normally attach. The SCR catalyst volume of 0.04 m^3 (1.5 ft^3) provided a space velocity of 10,000 hr^{-1} at a pressure drop of less than 1.5 cm (0.5 in) of water. Numerous runs demonstrated system repeatability and ease of operation.

Introduction

The 1990 Clean Air Act Amendments mandated reduced nitrogen oxide (NO_X) emissions for sources that have the potential to produce more than 22.7 metric tons (25 tons) of NO_X per year. Approximately 54,000 industrial, commercial, and institutional boilers currently in operation in the United States have been identified as sources that produce more than 25 tons of NO_X per year, presenting a need for low cost, high efficiency NO_X removal technologies.[1]

For NO_X control technologies to be applied to existing boilers they must be easy to operate and must not impair the efficiency of the boiler. Some NO_X reduction technologies include selective catalytic reduction (SCR), selective noncatalytic reduction (SNCR), low NO_X burners with advanced over-fired air (OFA), flue gas recirculation, and natural gas reburn which requires OFA in all cases.

This work attempted to develop and demonstrate a combined SNCR/SCR system for retrofit application to an oil-fired package boiler. The objective of the tests was to show that a typical package boiler can be effectively retrofit, optimized, and operated without using excessive manpower and controls. Successful demonstration of this technology will define an option for existing NO_X control sources and will likely provide redesign parameters for new applications. This type of SNCR/SCR system has been demonstrated on gas and coal systems at pilot[2] and full-scale levels. A catalyst housing was designed and attached where the access doors of the boiler normally attach. A honeycomb-type ceramic catalyst with square cells was installed in the catalyst housing. The SNCR system consisted of a water-cooled, two-fluid reductant injector nozzle that removed a large fraction of the NO_X and supplied reductant to the downstream catalyst.

Experimental

The Boiler and Retrofit

The SNCR/SCR system was retrofitted to a 590 kW (2-MMBtu/hr), three-pass, North American package boiler capable of oil and/or gas firing (see Figure 1). The first pass was the main fire tube, the second pass consisted of 24 6.4 cm (2.5 in) convective tubes, and the third pass consisted of 20 6.4 cm (2.5 in) convective tubes. The burner was a forced air burner located at the front of the boiler that used No. 2 fuel oil at an average rate of 53 L/hr (14 gal/hr) and 173 L/s (367 scfm) of air. Typical baseline operating concentrations were 107 ppm NO_X, 2.8% oxygen (O_2), 12.1 percent carbon dioxide (CO_2), 0 ppm carbon monoxide (CO), 0.6 ppm nitrous oxide (N_2O), and 174 ppm sulfur dioxide (SO_2). Generally, nitric oxide (NO) comprises more than 95% of the total NO_X, and NO was used for the NO_X numbers reported. The average gas flow estimated from the fuel consumption rate and the O_2 and CO_2 concentrations was 177 L/s (377 scfm), but a pitot tube velocity traverse 4 m (13 ft) downstream from the boiler measured 208 L/s (441 scfm); the difference is attributed to measurement error and in-leakage. The back of the boiler has an access plate that has a viewport, a thermocouple port, and a sampling/injection port, the latter centered axially on the 64 cm (25 in) diameter main fire tube. The SNCR reagent was injected countercurrent (toward the burner) through the sampling/injection port. Above and to the either side of the burner are access doors that expose the downstream ends of the second pass (first convective pass) tubes and the upstream ends of the third pass (second convective pass) tubes. The doors were removed, and the SCR catalyst housing was mounted where the doors were. A divider plate was installed to redirect the flow through the catalyst housing (Figure 2).

Sampling System

The sampling system consisted of four sampling lines: a pre-catalyst ammonia (NH_3) (NH_{3RES}) sampling train, a post-catalyst NH_3 (NH_{3SLIP}) sampling train, an SO_2 sample line, and a sample line for the continuous emission monitors (CEMs). The CEM sample system drew a slip-stream from the boiler and then pumped the sample to the CO_2, CO, O_2, and NO on-line analyzers as well as a gas chromatograph (GC) set up for N_2O measurement. N_2O can be a byproduct of the SNCR NO_X reduction system.[3] N_2O is currently not regulated on the Federal level as an air toxic; however, it is a contributor to global warming through the greenhouse effect. The sample gas for the CEMs passed through a Hankison chiller and was pumped through anhydrous calcium sulfate ($CaSO_4$) for removal of water subsequent to the chiller. The NH_3 measurement was aquired by pulling a slip stream of boiler gas through two 1 L impingers in series immersed in an ice bath. The first impinger contained 100 mL of 0.025 N sulfuric acid (H_2SO_4) solution that captured NH_3, and the second impinger was dry and followed by a dry gas meter. The impinger rinse was measured by an ion selective electrode to obtain the NH_3 concentration. The ion selective electrode was calibrated using at least three standards before each set of samples were analyzed, and a spike made from a separate stock was used to check the calibration before and after each sample set was analyzed.

SNCR

The system. The SNCR injector, reagent delivery/dilution system, and the SNCR reagent itself were supplied by Nalco Fuel Tech. The SNCR system consisted of a metering pump and an air atomized reductant injector nozzle. The reagent was similar to NO_XOUT A™, a Nalco Fuel Tech product that consists of 50% urea (NH_2CONH_2), approximately 50% water, and small amounts of anti-scalants and dispersants. The water and urea-based reagent were pumped to a mixing chamber where the total injected liquid amounted to 0.19 L/min (3 gal/hr). The water/SNCR reagent mix was delivered to the injector where it was atomized with air. The normalized stoichiometric ratio (NSR) of reagent nitrogen (N), NH_3, to baseline N, NO_X, was controlled by varying the flowrate of SNCR reagent. SNCR reagent feedrates were measured before and after every data set by pumping SNCR reagent from a burette instead of from the SNCR reagent reservoir barrel. The feedrates before and after the tests were consistent; however, the flow was not monitored during testing.

Optimization. SNCR reagent injection controlled all the post-installation optimization by providing the reductant for the SCR. NH_3, supplied by the breakdown of NH_2CONH_2, reduces NO_X in the presence of the catalyst. The objective when optimizing is to find the injection condition where SNCR removal is most efficient while ensuring that there is sufficient SNCR reagent to supply enough residual NH_3 (NH_{3RES}) for the catalyst to remove the residual, post-SNCR NO_X (NO_{XRES}). The ratio of these two values, NH_{3RES}/NO_{XRES}, defines the pre-catalyst stoichiometric ratio (SR_{RES}). Preliminary tests varied the amount of air, the injector insertion distance into the boiler, the type of nozzle at the tip of the injector, and the total flow of water at a fixed NSR. Although NO_X removal was greater at higher water flowrates, the flow was kept fixed at 0.19 L/min (3 gal/hr) to maintain sufficient boiler efficiency. The temperature profiles acquired before the retrofit indicated that the optimum SNCR injection temperature was close to the end of the main fire tube, but when the SNCR reagent solution and carrier gas were injected they introduced temperature gradients in the main fire tube that resulted in unexpected temperature profile results. The temperature profiles with the SNCR injection indicated that the temperature at the end of the main fire tube was much lower (680 °C) than optimum (about 900°C).[4] This can be attributed to the liquid from the SNCR reagent injection adhering to and then evaporating from the surface of the thermocouple, yielding a gas temperature measurement that is lower than the actual gas temperature. The optimum injector insertion distance for all nozzles, determined by the SNCR NO_X reduction (X_{SNCR}), was between 0 and 20.3 cm (8 in) from the back end of the boiler.

Six different nozzles were tested: three nozzles had round-orifice diameters of 0.1 (0.0388), 0.2 (0.0775), and 0.4 cm (0.155 in) that provided a cone spray pattern; one nozzle had six 0.18 cm (0.07-in) holes evenly distributed 0.28 cm (0.11 in) from the center of the nozzle that provided a cloud spray pattern; one nozzle had an oval orifice that created a fan spray pattern; and one had an oval orifice at a 45° angle to provide an angled fan spray pattern. In the boiler, both fan spray nozzles performed better than the cloud spray, which, in turn, performed better than the cone spray nozzles. The optimum settings for air pressure and injector distance from the end of the boiler were different for all the nozzles except the two fan spray nozzles. The angled fan spray with the angle pointing up was determined to be the best nozzle to use. The removal was greatest with the injector tip 3.8 cm (1.5 in) from the end of the boiler, and the air at 241 kPa (35 psi). The factors that went into determining the best nozzle were the combined SNCR and SCR total NO_X reduction (X_{TOT}), NH_{3SLIP}, and N_2O emmisions.

SCR

The SCR catalyst was a commercially available titanium and vanadium ceramic catalyst with 7.6 square cells/cm^2 operating at a nominal level of 10,000 h^{-1} space velocity [standard temperature and pressure (STP)]. The catalyst did not appear to degrade over about 240 hours of operation; it also did not collect soot despite overnight shutdown and morning re-start for each test, which could cause temperature changes and increase sooting during startup. Sometimes NH_3 can combine with sulfur trioxide (SO_3) to form ammonium sulfate [$(NH_4)_2SO_4$]. Catalysts can contribute to this formation by converting SO_2 to SO_3. No drop in SO_2 was observed across the catalyst and no NH_3 salts were evident in the boiler. The pressure drop across the catalyst was measured by a manometer and by a Magnahelic pressure gauge to be nominally 1 cm (0.4 in) of water.

Boiler Operation

The boiler was always operated at full load. It was started and run for 3 hours with just water and air injected through the injector to establish temperature, NH_3, and NO_X equilibrium. Then the baseline (no reagent) readings were taken and it was run for 3 more hours with the SNCR reagent flowing. After 3 hours of equilibration time, NH_{3RES}, NH_{3SLIP}, and CEM measurements/samples were recorded. The system was allowed 1 hour to return to equilibrium and post-test baseline readings were taken.

Results and Discussion

The SNCR system typically removed 30 to 40% of the NO_X. Figure 3 shows X_{SNCR} and the resultant SR_{RES} for varying NSR values. The data points are all using the angled fan spray nozzle with the nozzle tip located 1.5 in from the back wall of the boiler. Variation of NSR from 1 to 4 shows little effect on X_{SNCR} and no consistent trend for SR_{RES}.

The SCR NO_X removal performance versus SR_{RES} is shown in Figure 4. The catalyst shows consistent NO_X reduction (X_{SCR}) trends with increasing SR_{RES} until SR_{RES} reaches values above approximately 0.7, where X_{SCR} levels off at about 80%. This is a fairly typical trend for a catalyst performance The points on Figure 4 are a compilation of both fan spray nozzles.

The ratio of the decrease in NO_X to the decrease in NH_3 averaged 1.33/1 across the catalyst. This is usually a 1/1 ratio. NH_3 measurements that are too low (due to NH_3 breaking through the impingers, or due to dry gas meter calibrations returning sample volumes that are higher than actual) could cause the ratio to seem higher than 1/1.

While NSR has little effect on X_{SNCR}, and due to the wide range of testing conditions reported, no obvious relationship with SR_{RES} (Figure 3), the appropriate SR_{RES} (> 0.7, from Figure 4) is probably obtained at NSR values around 2 or higher. This is more clear from Figure 5, which shows the system's total NO_X removal, X_{TOT}, versus NSR. This shows that under optimal conditions this retrofit established NO_X reduction of 93%. All ammonia slips were less than 6 ppm, so there is clearly enough catalyst to remove the residual NH_3 from the SNCR process.

N_2O formation increases with increasing NSR values (Figure 6). Under fairly typical operating conditions of NSR = 2, measured N_2O emissions are about 10 ppm. These values have not been accounted for in prior NO_X reduction percentages.

The sometimes large degree of scatter in the data are indicative of the varied SNCR chemical injection rates. Practical operation of an SNCR/SCR system would involve finding the optimum conditions for each specific boiler and operating within those conditions. Shakedown, optimization, and long-term operation of this system are ideally suited for a neural network feedback/control or fuzzy logic control system.

Conclusion

An SNCR/SCR hybrid system retrofit to an oil-fired package boiler had an apparent optimum NSR around 2 where 85% NO_X reduction could be achieved without exceeding 6 ppm NH_{3SLIP}. N_2O formation was generally below 15 ppm. At the optimum NSR, it was nominally 10 ppm.

The SNCR/SCR hybrid system was easily retrofit to our existing oil-fired package boiler. Although the design of the SCR catalyst housing was specific to this boiler, similar designs could be developed for other units. Equipping new boilers via minor design changes would probably be even easier and more effective than retrofitting old ones. Once the system is installed, optimization time may be about 1 or 2 days. Changes in temperature profiles may make optimization difficult. Current work is developing a fuzzy logic control system to counter this.

Further testing may be needed to assess long term boiler effects and long term catalyst durability to determine added costs from reagent use and catalyst replacement.

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Nomenclature

NH_{3RES}	The residual ammonia in the boiler after the SNCR reaction measured before the catalyst.
NH_{3SLIP}	The residual ammonia in the boiler measured after the catalyst.
NSR	The normalized stoichiometric ratio of input nitrogen (from the SNCR reagent) to the nitrogen in the boiler in the form of NO_X.
NO_{XRES}	The residual NO_X in the boiler after the SNCR reaction measured before the catalyst.
SCR	Selective catalytic reduction.
SNCR	Selective noncatalytic reduction.
SR_{RES}	The stoichiometric ratio of the post-SNCR residual reagent nitrogen, NH_{3RES}, to post-SNCR residual nitrogen measured before the catalyst, NO_{XRES} .
X_{SCR}	The percent reduction of NO_X across the catalyst.

X_{SNCR} The percent reduction of NO_X from baseline level to the NO_X level measured after the SNCR reaction before the catalyst.

X_{TOT} The percent reduction of NO_X from baseline to the NO_X level measured after the catalyst.

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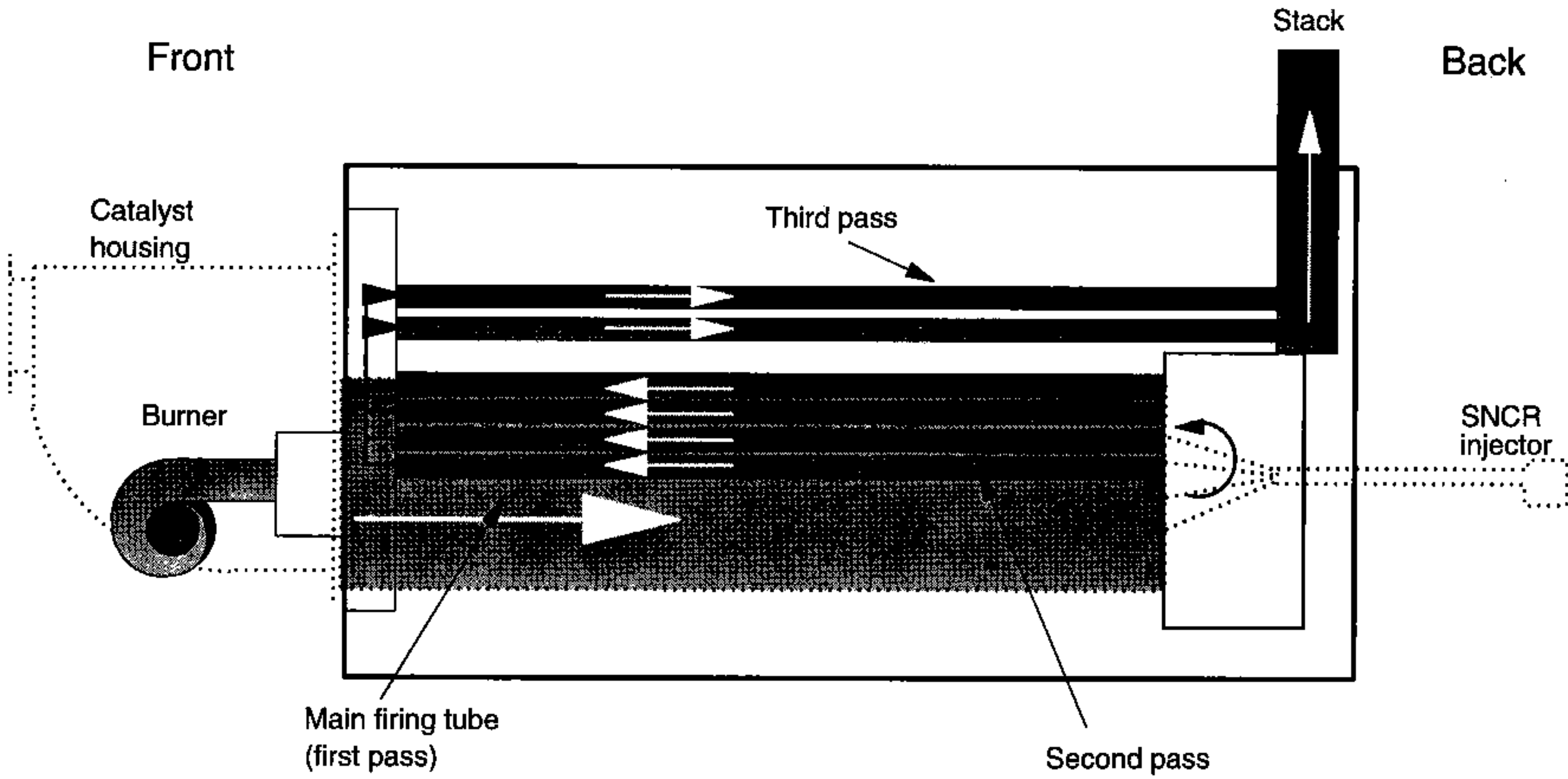

Figure 1. The North American package boiler side view with SNCR/SCR retrofit outlined by dotted lines.

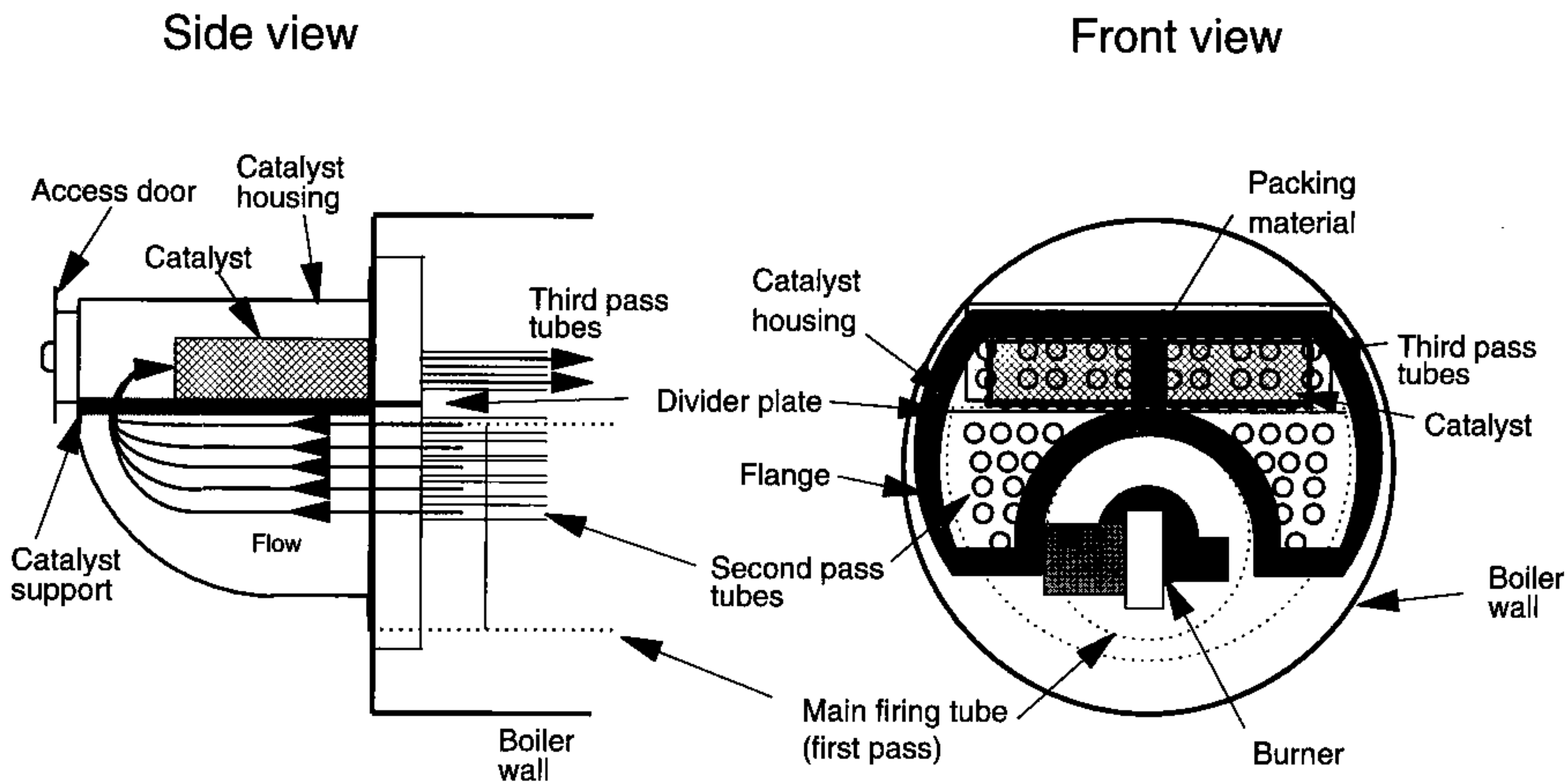

Figure 2. SCR retrofit diagram.

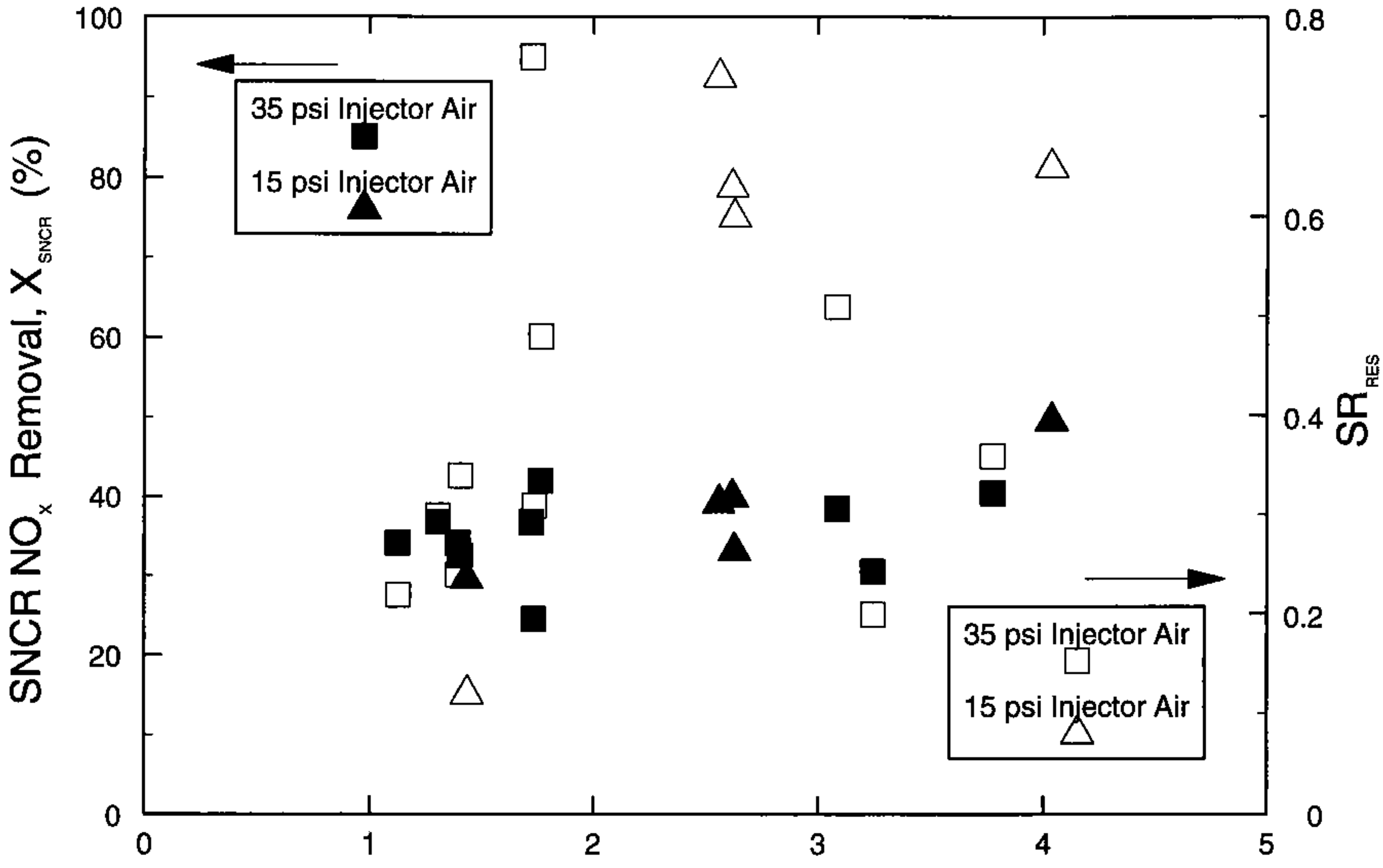

Figure 3. SNCR system performance. Angled fan spray nozzle with injector tip 1.5 in from the back of the boiler.

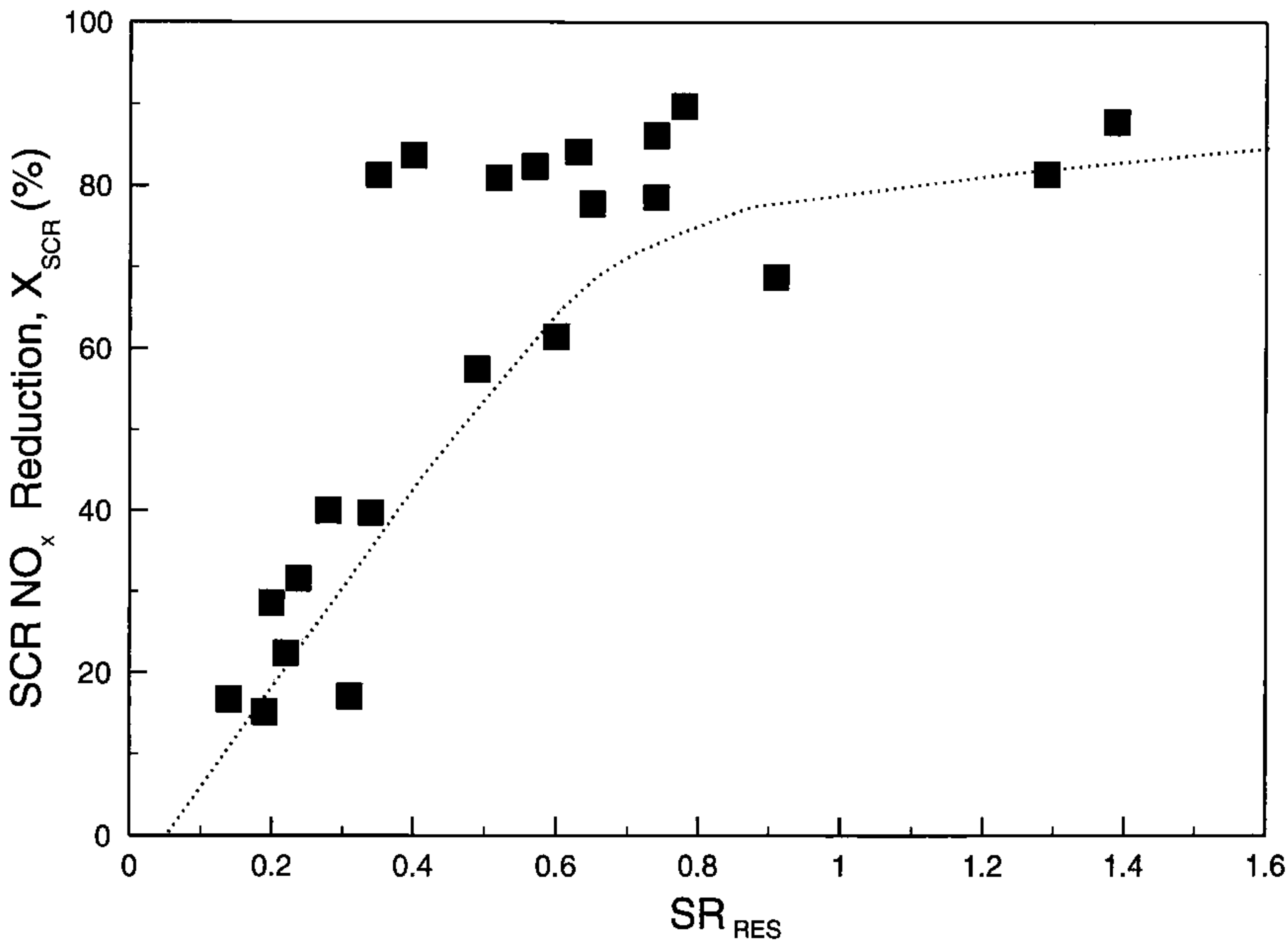

Figure 4. NO_x reduction across catalyst for varying SR_{RES}. NH_{3RES} is between 10 and 55 ppm.

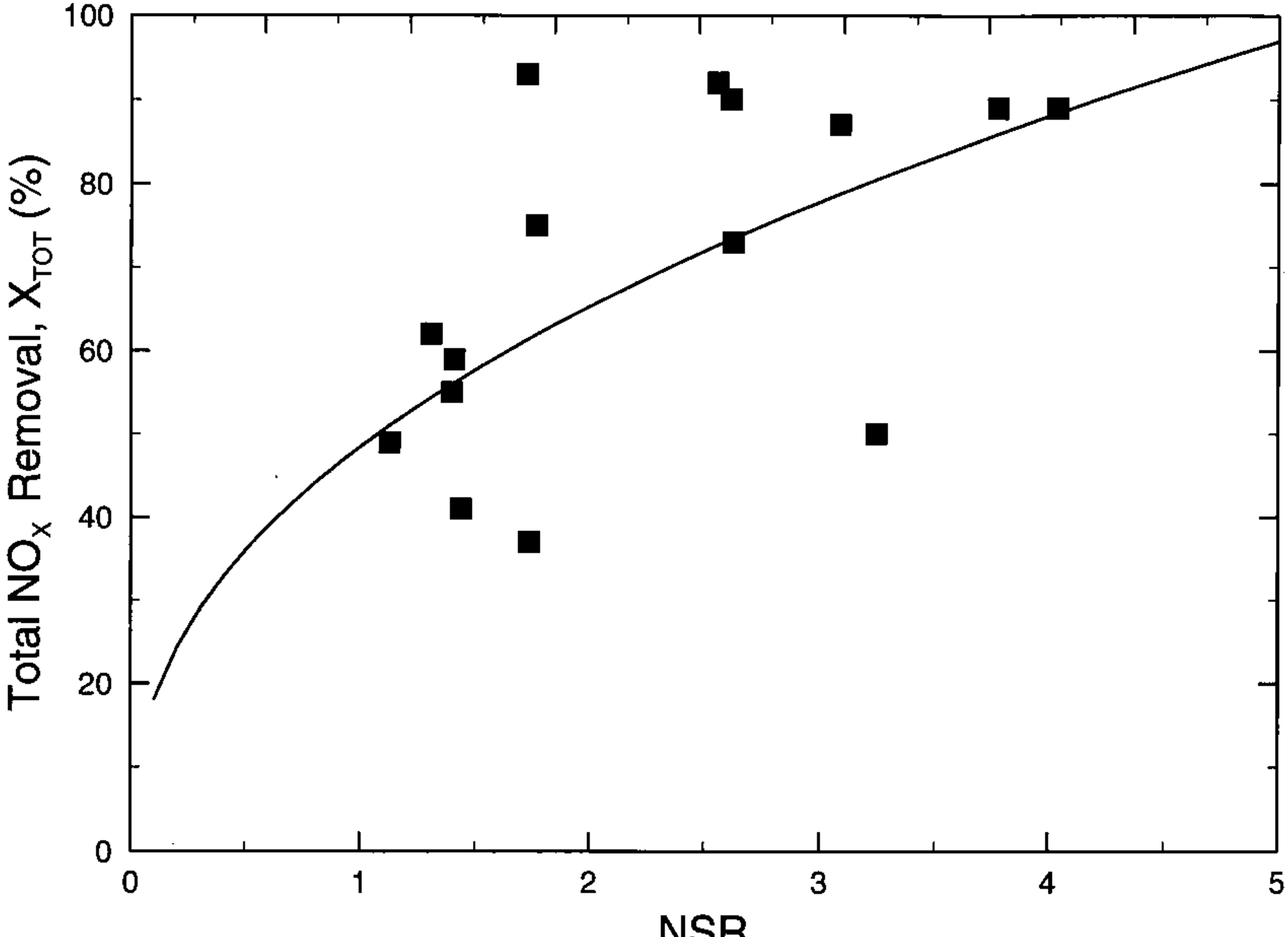

Figure 5. NO_x reduction for varying NSR. Angled fan spray nozzle data only.

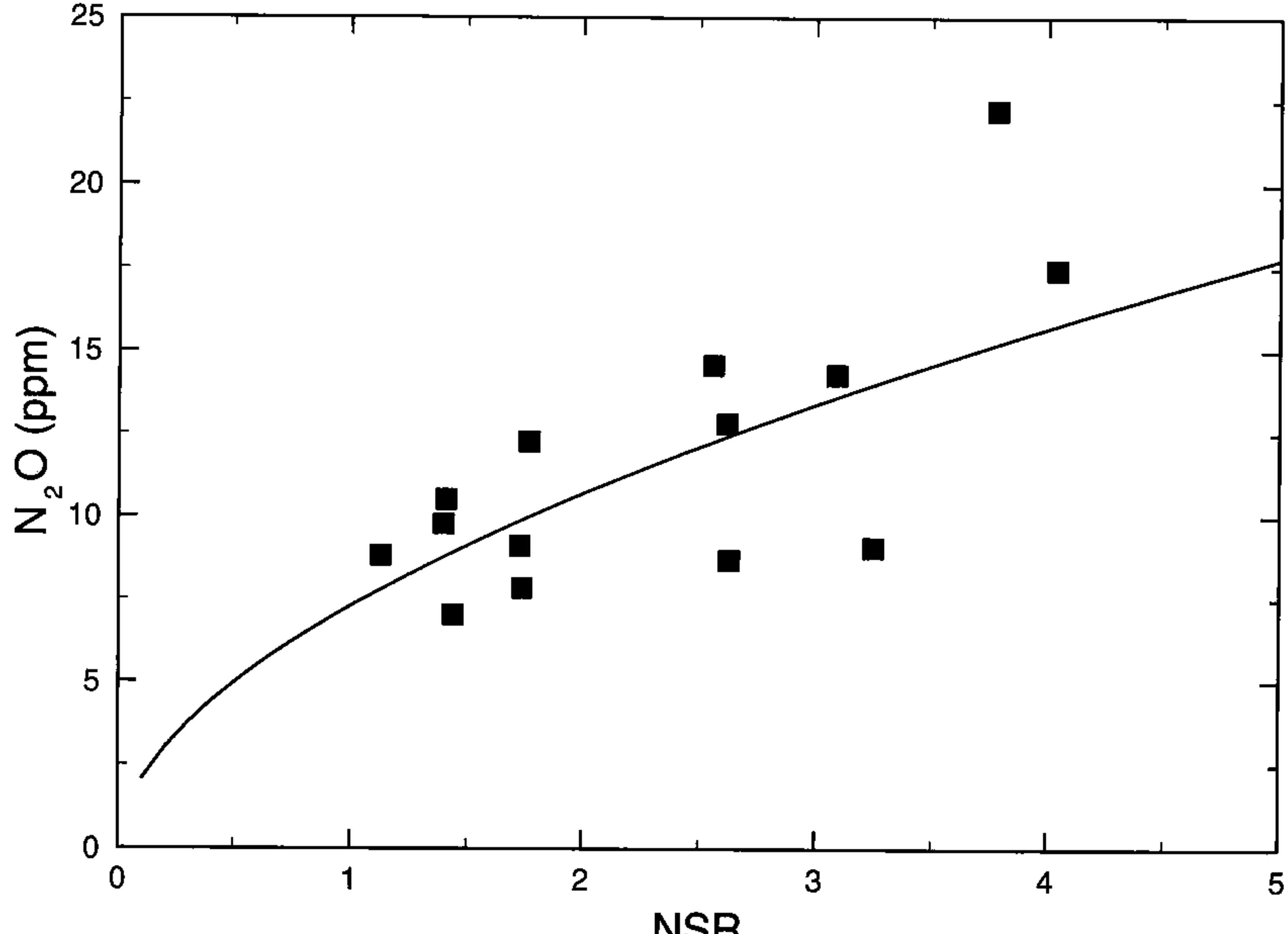

Figure 6. N_2O reduction across catalyst for varying NSR. Angled fan spray nozzle data only.