Hybridization of Urea-SNCR with SCR
A Fit for the Future

V. Albanese, J. Boyle, W. Sun
FUEL TECH, INC.
Batavia, IL

R. Abrams
BABCOCK POWER
Worcester, MA

ICAC's Clean Air Technologies & Strategies Conference
March 7-10, 2005
Baltimore, MD

Abstract

Currently, SNCR/SCR Hybrid systems have been installed in utility and industrial furnaces as both commercial and demonstration projects. In one application, a small, in-duct catalyst bed was added for catalytic reduction and for the removal of ammonia slip. In another, a large SCR reactor was used to provide as much as 90% reduction while the SNCR system provided both ammonia reagent to the catalyst and additional NOx reduction. In industrial applications, the system is frequently designed to provide a sliding scale of SNCR and/or SCR NOx reduction as operating conditions and the required NOx reduction varies.

In all instances, the Hybrid systems have provided significant improvement in the efficiency of chemical utilization, as compared to conventional SNCR, and increased NOx reduction as compared to the performance of the In-duct SCR standing alone. These improvements result in a lowering of the operating costs for the SNCR system. In addition, SO_2 oxidation and gas side pressure drop will be decreased as compared to an equivalent SCR. Used correctly, this lessens the risks associated with both ammonium bisulfate formation and plume opacity associated with SO_3.

A new utility application is currently in design that will provide 65% overall reduction using a Fuel Tech, Inc. urea-SNCR system with downstream mixing and an in-duct catalyst reactor by Babcock Power. The integrated system is being designed through the use of advanced computational fluid dynamics and cold flow modeling techniques.

Introduction

In the last decade or more, boiler owners and operators have been investigating techniques for the reduction of NOx from their stack emissions. A wide range of options are available for effective control between the burner zone, in which the NOx is formed, to the final emission at the stack. These options include fuel switching, combustion modifications such as low NOx burners, over-fire air (OFA), and rich-reagent injection (RRI) in the combustion zone as well as post combustion processes such a gas re-burn (GR), selective non-catalytic reduction (SNCR), and selective catalytic reduction (SCR).

Each of these control technologies has inherent capital and operating costs that vary with site specific factors, and each has potential balance-of-plant concerns. In addition, many of these technologies interact with each other. Changes in the fuel may require design modifications in post-combustion controls such as GR, SNCR and SCR systems. Changes to the flame stoichiometry may lead to increased CO, unburned carbon and ash properties that can also affect post combustion controls.

Potentially, two or more available means of NOx control can be compatibly combined to reduce NOx wherein the end result is more cost effective than the sum of its parts. Hybrid combinations of SNCR and SCR are a particularly flexible method for effecting moderate to deep reductions of NOx at cost ranges typically below those of a fully-engineered SCR retrofit.

This paper presents a discussion of SNCR/SCR hybrid theory and design. An example is used to step through the design process for SNCR and elaborate the design modifications required to create an SNCR/SCR hybrid system. The discussion will not include the possible effects of combustion zone modifications on this combined technology. In general, however, it is assumed that the responsible utility client has already investigated and, in many cases, implemented technologies to reduce the formation of NOx in the combustion zone.

Two utility field installations will be reviewed that illustrate possible design strategies. In the first case, an existing SNCR system was modified to work with a full-size SCR for demonstration/test purposes. In the second, a small SCR was in a slightly modified duct for the purpose of ammonia slip reduction.

In both cases, significant co-benefits were seen. The utilization of the SNCR process was enhanced and the overall NOx reduction was increased. The required reactor size was dramatically smaller than the equivalent SCR volume necessary to achieve the same NOx control performance.

SNCR/SCR Hybrid Theory

The Hybrid SNCR/SCR process is more than a combination of an SNCR and downstream SCR. Although it can be as simple as a combination, the term “hybrid” refers to a blending that leaves both of the original technologies improved to work, and by working, with each other. The new process provides improvements in chemical utilization and overall NOx reduction. The two

NOx reduction technologies each provide process strengths which make the hybrid combination more flexible and effective than the sum of its parts.

Selective Non-Catalytic Reduction (SNCR) is typically applied in the furnace, where relatively high temperatures serve to initiate the breakdown of urea to form the transient species which lead to effective NOx reduction. The technology is limited to temperatures high enough to insure very low ammonia breakthrough. At very high furnace temperatures, however, performance can be lessened by competing reactions which either consume effective chemical or lead to NOx formation. The hybridized SNCR takes advantage of a downstream "ammonia sink" by injecting chemical in cooler regions where NOx reduction and chemical utilization improve dramatically. One of the most limiting factors of the SNCR process has been removed.

Selective Catalytic Reduction (SCR) is typically performed in much cooler flue gas passes where the oxidation potential of nitrogen species is minimized. The catalytic surface provides sites which permit the ammonia and NOx to react at nearly perfect utilization. The extent of NOx reduction is often limited by the local ammonia to NOx ratio, the flue gas temperature, the size of the catalyst reactor and the permissible un-reacted ammonia "slip". The catalyst size is limited by the available space, the resulting gas-side pressure drop, the oxidation of SO_2 to SO_3, and the size of the capital investment required for construction. Obviously, all of these limitations are linked with other station-specific requirements such as the expected life of the unit, the applicable NOx regulations and markets, the choice of fuel and the complexity of retrofit applications.

The hybridization of SNCR and SCR utilizes a more favorable low-temperature SNCR injection to provide substantially improved NOx reduction and increased utilization of the injected urea solution to minimize operating cost. The improved performance also produces an increase in the resulting ammonia slip. The ammonia slip feeds a compact or in-duct SCR reactor which utilizes the slip to further reduce NOx while limiting the costs associated with a larger catalyst. For example: a hybrid SNCR/SCR system may achieve 65% to 75% overall NOx reduction. The improved SNCR system would provide 50% reduction, a substantial increase from the 25-35% available with strict ammonia slip control. The downstream SCR would then provide an additional 30% or greater reduction, requiring less than one third the catalyst volume required for an equivalent 65% SCR reduction. The smaller catalyst converts proportionally less SO_2 to SO_3 and decreases the pressure drop by the same fraction.

Chemical Utilization

In post-combustion NOx control processes, NOx reduction is achieved at a given Normalized Stoichiometric Ratio, or NSR. Simply put, NSR refers to the ratio of chemical reductant applied to the amount of NOx existing in the flue gas. With SCR, ammonia is typically the reductant and is typically applied at an NSR of one for deep reductions. In other words, one mole of NH_3 is applied per mole of NOx. If only a 75% NOx reduction was required, the NH_3 NSR would be approximately 0.75. In non-catalytic systems, the reductant is applied in broader ranges of NSR because of relatively lower NOx reduction efficiency compared to catalytic systems. In commercial practice, the NSR ranges from 0.6-2.0.

Chemical utilization is a quantification of NOx reduction efficiency expressed by:

$$\text{Utilization [\%]} = \text{NOx Reduction [\%]} / \text{NSR}$$

In other words, if each lb-mole of injected urea or ammonia reduces NOx to the theoretical maximum amount, utilization is 100%. One hundred percent chemical utilization is approached in SCR systems, but in SNCR system values range from 30-60%. In commercial post-combustion NOx control systems, maximizing utilization, all other things being equal, minimizes life cycle operating costs.

Hybrid Utilization

Figure 1 schematically depicts the enabling effect of a downstream SCR catalyst bed on SNCR performance in a hybrid system. SNCR NOx reduction occurs in a defined temperature window, roughly bell-shaped with maximum SNCR NOx reduction occurring at the top, or plateau of the bell. In a commercial "stand-alone" SNCR system, performance is optimized by operating on the "right side of the slope", area A in the temperature window curve. In this region, the hot side of the performance maximum, ammonia slip is very low or non-existent. This is often an operating constraint imposed by the source owner. In contrast, the SNCR component of the hybrid system operates best at the plateau, where the temperature is lower. In this region (Area B), SNCR NOx reduction is higher and some ammonia slip is produced. The ammonia slip is available to reduce NOx in a catalyst system downstream. When operated in this manner, SNCR NOx reduction is maximized and additional NOx reduction occurs in the catalyst portion, fueled by the generated ammonia slip.

Hybrid systems can also be designed to operate in the cooler zone (Area C - the "left side of the slope") which will produce more ammonia slip than the other regions. In this scenario, SNCR NOx reduction is less than maximal and SCR NOx reduction increases until limited by catalyst space velocity. This condition may exist in some applications where a drop in unit load is accompanied by decreased gas temperatures and flow rates. In most cases, however, the decreased load condition provides an opportunity for deeper SNCR reductions as well.

Hybrid systems can be designed to maximize SNCR performance while "existing duct" SCR controls the ammonia slip (Area B). Reagent utilization for NOx reduction can increase dramatically compared to stand-alone SNCR, as discussed above. Therefore, reagent cost per unit of NOx reduced is lower with the hybrid system than with the stand-alone SNCR. Current operators of SNCR systems consider these questions in the design stage for prospective hybrid systems:

- What is the expected additional reduction of NOx for a constant urea (reagent) flow?
- What is the expected reagent flow reduction for constant NOx reduction?

SNCR System Design

The first step in the Hybrid design process is a complete assessment of the subject unit through customer surveys, unit drawings and data analysis. Generally, all retrofit applications are visited and, when possible, temperature and gas species mapping is obtained across the load range. This data is used to tune a complete analysis by computational fluid dynamics (CFD) and chemical kinetics (CKM) modeling.

For illustration purposes, a 125 MW front-fired pulverized-coal boiler has been used as an example and is discussed here. The CFD model has been completed at full load and a side-sectional temperature profile of the upper furnace is shown in Figure 2. The gas temperature at the nose averages about 2150 degrees F. This is not unusual for a unit this size. Although furnace exit gas temperatures on units from 80 MW to 800 MW may vary between 1800 F and 2700 F, the analysis process described here is similar and applicable to all units.

Once the CFD modeling has been performed for each subject case (unit load, fuel type, degree of air-staging, etc.), chemical kinetics modeling is completed for a representative set of streamlines generated from the result. One set of analysis results is shown in Figure 3, for an assumed CO concentration of 250 ppm at the point of chemical release and an NSR of about 1. The results show that significant potential NOx reduction can be obtained with chemical treatment at 1900F.

In fact, the standard SNCR (ammonia slip limited) design case will assume that ALL chemical must be released before 1850F, to limit the resulting ammonia slip. This will lead to a higher average release temperature and less than theoretically optimal performance. A typical SNCR wall-injection zone is shown in Figure 4. Also shown is a semi-transparent surface indicating the ammonia slip limit temperature of 1850F. The actual NOx reduction achieved will depend on the mass-averaged release temperature of all droplets and the net coverage of the furnace gas.

Theoretically, if the average release temperature is 2000F and the net coverage is 60%, the final NOx reduction will be about 34%. This will actually depend on the mass averaged values integrated over the gas flow and, in the final analysis, field optimization and tuning.

Hybrid SNCR System Design

The SNCR design example is continued in Figure 5. In this case, the previous figure has been over-laid with the results of the CKM analysis. The colored bands of potential NOx reduction increase from 0% near the nose to more than 60% at the ammonia slip limit surface and then gradually back down to 0% in the convective pass. The CKM results vary within the furnace as the low temperature limit is approached, and so this figure should not be interpreted precisely, but as a guide to potential average performance.

The hybrid SNCR system, with the downstream SCR reactor, provides chemical injection without strict regard for the ammonia temperature limit surface. A new injection strategy is shown in Figure 6 and consists of wall-injectors placed higher in the furnace and two multiple-nozzle lances (MNLs) that provide coverage at the entrance to the convective pass.

In this case the average chemical release temperature has dropped to approximately 1850F, by design. If the assumed chemical coverage remains the same as above, the expected NOx reduction increases to 42%. In fact, the hybrid system injection design is free to push the maximum coverage without strong regard for ammonia slip and this will result in even higher SNCR reductions. In this example case, as much as 50-55% NOx reduction might be possible.

In addition to this dramatically increased NOx reduction, the resulting ammonia slip will travel downstream to an SCR where additional NOx will be removed from the gases. A small SCR, capable of perhaps only 40% reduction in NOx, would lead to an overall reduction of more than 70% without additional chemical. The SCR reactor system, therefore, must be capable of taking a non-homogeneous mixture of ammonia slip and residual NOx and providing the necessary ammonia and NOx control.

SCR Reactor System Design

Babcock Power is the leading technology designer for utility Selective Catalytic Reduction (SCR) systems in North America. Babcock Power designed and built the largest Selective Catalytic Reduction system operating in the world. They have experience with a wide range of fossil fuels including Powder River Basin Coal, refinery bottoms, Pet Coke, and high sulfur coals. Babcock Power also has the technology base to design Selective Catalytic Reductions for fuels with high levels of catalyst poisons including arsenic. This technology has been used in over 40,000 MWs of SCRs operating in the US. This broad base of experience provides Babcock Power with the expertise to furnish SCR systems, including in-duct SCRs, that are reliable, flexible in operating parameters and meet current economic and environmental challenges.

Mixing Technology

One of the primary technology advantages that Babcock Power offers is the application of the proprietary Delta Wing® Technology. The application of this technology to SCR installations allows both gas mixing and reagent injection in one simple application, with no moving parts in the gas stream.

It is quite common to have temperature or constituent concentration differences in any flow stream. A typical non-uniform flow stream would be the flue gas leaving a boiler with less than a full complement of burners in service. For example, the temperature or oxygen concentration can be different from side-to-side exiting the boiler even though the gas has passed through tube bundles and been in a turbulent flow regime. This turbulent gas flow does not necessarily generate homogeneous flue gas.

The Delta Wing® mixer receives this boiler exit gas and smoothes all gas characteristics: temperature, oxygen concentration, dust concentration, NOx concentration, ammonia concentration, SO_3 concentration, etc. The mixer itself is a stationary obstruction in the duct, usually a disk or triangular plate, oriented at a slant to the flow direction. Upstream of this device is turbulent but not necessarily homogeneous flue gas. Immediately downstream of this device are large violent vortices. The duct may have four or five mixers over a 40-foot wide duct and the resulting vortices cover the whole cross sectional area of the duct.

Application of this mixing technology has been completed for a compact or in-duct SCR bed where significant duct modifications were not desired. CFD modeling of this case is shown in

Figure 7. As is shown in the figure, if the test model of the system indicates it is necessary, a second set of mixing devices can be added downstream of the first set, usually at a 90° turn just before the reactor. The result of these vortices, as they flow downstream and mix with adjacent vortices, is a well-mixed gas.

These vortices consistently form in relation to the mixing device size, position, and orientation in the ductwork system. Because of this, Babcock Power is assured of two key things:

1. The vortices can be well modeled, i.e. predetermined, in a 3D model based on a scaled geometry of the ductwork system and mixing device size, position and orientation.
2. The vortices are not dependent on gas flow quantity and therefore will consistently form over a wide range of gas flows and boiler outlet conditions.

These two key factors have been proven numerous times by scale models used in all of our projects and by the close correlation between the "modeled" and "real world" performance measurements in the actual installations. Figure 8 is a photograph of the cold-flow model used to validate the CFD model described previously. These two models are used together to achieve a final design solution. The Delta Wing® technology has consistently performed well over a range of gas flows exceeding the normal turndown range of the boiler and is a key factor in the success of in-duct SCR reactor systems.

Field Testing – Mercer Station

The NOxOUT SNCR/SCR Hybrid process was tested at Public Service Electric and Gas, Mercer Station. The unit, which had an existing SNCR system, was partially retrofitted with an expanded duct catalyst as part of a study of SCR, combined SNCR-SCR, and Hybrid SNCR/SCR. In this preliminary work it was shown that deeper than design reductions in NOx were possible through modification of the SNCR system with less than design chemical (urea) flow rates. This was achieved by decreasing the effective chemical release temperature in the furnace. Specifically, the chemical flow rate was decreased by one third while maintaining the same SNCR performance. This represented a 50% increase in chemical utilization.

The by-product of this temperature shift, breakthrough ammonia slip, was utilized in the SCR reactor where further NOx reduction was achieved and ammonia slip levels were reduced to within acceptable limits. The SCR reduction was varied from 16% to 55%, simulating various possible reactor configurations. In each case, the overall chemical utilization was more than doubled. Although the SCR reactor was large enough to provide greater than 85% NOx reduction on its own, it was shown that ammonia and NOx distributions to the catalyst were sufficiently uniform to allow for a substantial reduction in catalyst volume without adversely affecting the process.

A static mixing grid at the economizer exit was part of the original program scope. This mixing grid, as well as natural and turbulent diffusion in the back pass of the unit, provided sufficient mixing of the ammonia and NOx in the flue gas to achieve as much as 84% reduction at full load and more than 90% reduction at low load.

Commercial Demonstration - Seward Station

A commercial hybrid SNCR/SCR system was designed, constructed, and installed for GPU GENCO, at Seward Station. This unit was a C-E, coal burning, tangentially fired boiler rated at 148 MWg. The unit was designed to operate between 50% and 100% MCR. A commercial urea-based SNCR system had been previously installed on this unit and it provided NOx reduction from 0.78 lb/10^6 Btu to 0.45 lb/10^6 Btu with less than 5 ppm slip.

High concentrations of SO_3, cool air pre-heater exit temperatures and significant air in-leakage before the air pre-heater combined to make this installation particularly sensitive to ammonium salt formation. Prior to the SCR installation, the SNCR system was tuned to operate at less than 2 ppm ammonia slip by shifting much of the chemical injection from the convective pass lances to the wall injection zones. The resulting controlled NOx was 0.50 lb/10^6 Btu. Although the system operated at this slip level with no problem, additional NOx reduction was desired and a decision was made to pursue a hybrid SNCR/SCR system. This decision was further supported by limited test data showing NOx emissions as low as 0.36 lb/10^6 Btu (54% reduction) with an associated ammonia slip of about 10 ppm.

Construction was completed as a commercial demonstration with GPU Genco, the US Department of Energy and Fuel Tech Inc., as well as two independent catalyst vendors. A static mixing grid and turning vanes were utilized to decrease the known and predicted gas and solid flow imbalances in the unit. Flue gas mixing and turning vanes were also designed to reduce temperature variations and eliminate the localized cool spots due to air in-leakage. Design of these duct internals was completed using both computational fluid dynamics (CFD) and cold-flow models.

Unlike a traditional SCR system, the catalyst design was based primarily on the efficiency of ammonia removal. Catalyst formulations were selected to minimize the oxidation of SO_2 to SO_3, and to provide minimal pressure drop. The NOx reduction was expected to vary across the face of the catalyst, depending on the available ammonia slip. The ammonia removal was designed to insure that even the highest concentrations of ammonia in the well-mixed gas stream would be reduced to less than 2 ppm at the catalyst outlet.

This first commercial installation was completed after some design modifications to address low-load temperature swings and high arsenic coal. Some of the catalyst was replaced with a design more suited for high dust application. The final configuration operated successfully until the unit was decommissioned in the spring of 2004.

System Design

As the examples above illustrate, Hybrid SNCR/SCR NOx reduction systems can be engineered in several forms. It is possible to install a commercial SNCR system for furnace reductions of NOx, and install a conventional SCR system downstream of the economizer on the same unit for removal of the remaining NOx, and enjoy deep levels of NOx reduction with the combined system. For the purpose of semantic clarity, one might consider the foregoing system “combined

SNCR/SCR" while reserving the "hybrid" description for units which utilize the ammonia slip from an improved SNCR process as the NOx reductant entering the downstream SCR.

Hybridized SNCR/SCR can assume several configurations depending upon the level of overall NOx reduction desired and the unit configuration. The SNCR system can be used as the primary source of reduction with an in-duct or air-heater SCR, as a trim to a relatively large SCR, or anywhere in between the two. The role and relative productivity of the SNCR system can be adjusted automatically as the daily load variations, fuel modifications, or even seasonal NOx requirements change. The combined factors lead to differences in the desired catalyst volume and, therefore, to the catalyst contribution to the total capital requirement.

It is important to view the potential design and application of hybridized SNCR/SCR from an economic standpoint. Besides assuming several physical configurations, hybrid SNCR/SCR can be operated in different ways. Among the many considerations for the choice of designated hybrid operation are:

- What is the desired level of NOx reduction?
- Are the NOx reduction requirements incremental and/or variable?
- What are the NH_3 slip and SO_2 oxidation constraints?
- What volume catalyst can fit in the existing ductwork where face velocity will be within catalyst manufacturer specifications?
- What level of additional pressure drop is tolerable by the present fan?
- What structural steel/ductwork changes must be made to support the catalyst?

It is obvious that total capital requirement for the catalyst retrofit will increase as the catalyst size and retrofit complexity increase. The key to minimizing life cycle NOx reduction costs is to find the appropriate balance between annualized capital charges and operating costs for the remaining life of the system. The challenge for SCR retrofit is to minimize the capital requirement. The challenge for SNCR use is minimization of reagent required. Designing hybrid SNCR/SCR systems suggests optimization of these costs over the life cycle for a specific level of NOx reduction.

Life-cycle Costs

The use of hybrid SNCR/SCR systems permits "tailoring" NOx reduction and life-cycle cost to the potentially complex future requirements of NOx reduction for ozone mitigation. The total life cycle cost of the modified SNCR/SCR NOx reduction process is a function of chemical utilization, catalyst size and capital requirement. Very high NOx reductions, of perhaps 90%, require a substantial catalyst volume. This system cannot be placed in existing duct dimensions and will always require, at the very least, major modifications.

A modified SNCR/SCR process would conceptually be effective for approximately 75% overall NOx reduction. Precatalytic SNCR reduction of 50-60% requires only 38-50% SCR reduction, and only 57% of the catalyst volume required for stand-alone SCR targeted at 75% overall reduction. An "in-duct" catalyst may be used on a site-specific basis to fulfill this half-sized volume requirement.

The Seward station SNCR/SCR hybrid system, described above, was operated seasonally to provide maximum NOx reduction during the summer ozone-season. The reduced capital, as compared to an equivalent SCR, provided for a low operating burden when the system was not in use. The chemical portion of the operating expense is “shut-off” when the system is off-line.

Hybrid SNCR/SCR represents more than a simple combination of two NOx control strategies. The hybridized systems provide high levels of NOx reduction with operating costs lower than traditional SNCR and capital costs well below traditional SCR.

Two hybrid systems are currently being operated in the steel industry where urea-SNCR injection is used both to provide highly efficient NOx reduction in the injection zone and to provide a stream of ammonia as feed to an in-duct SCR reactor.

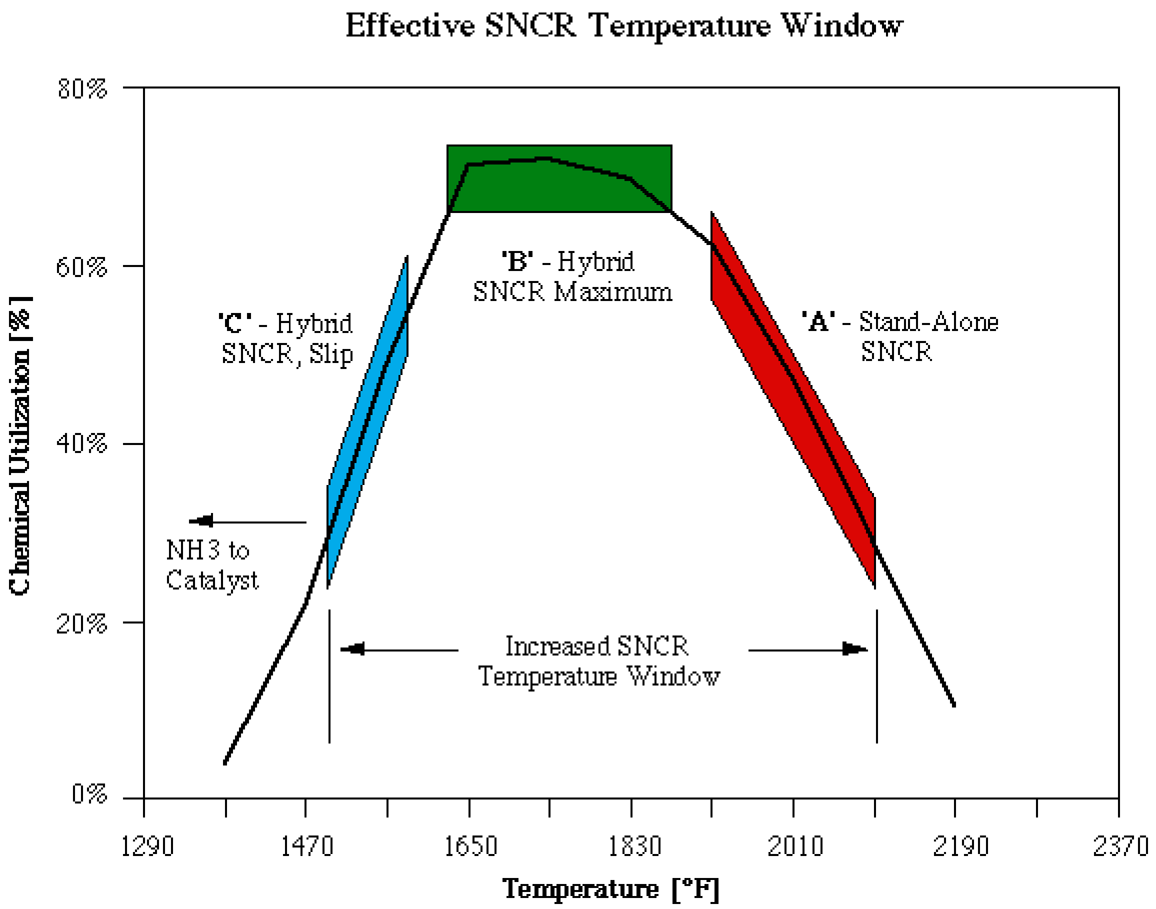


Figure 1. Hybrid SNCR/SCR yields improved performance.
Total reagent utilization approaches 100 %

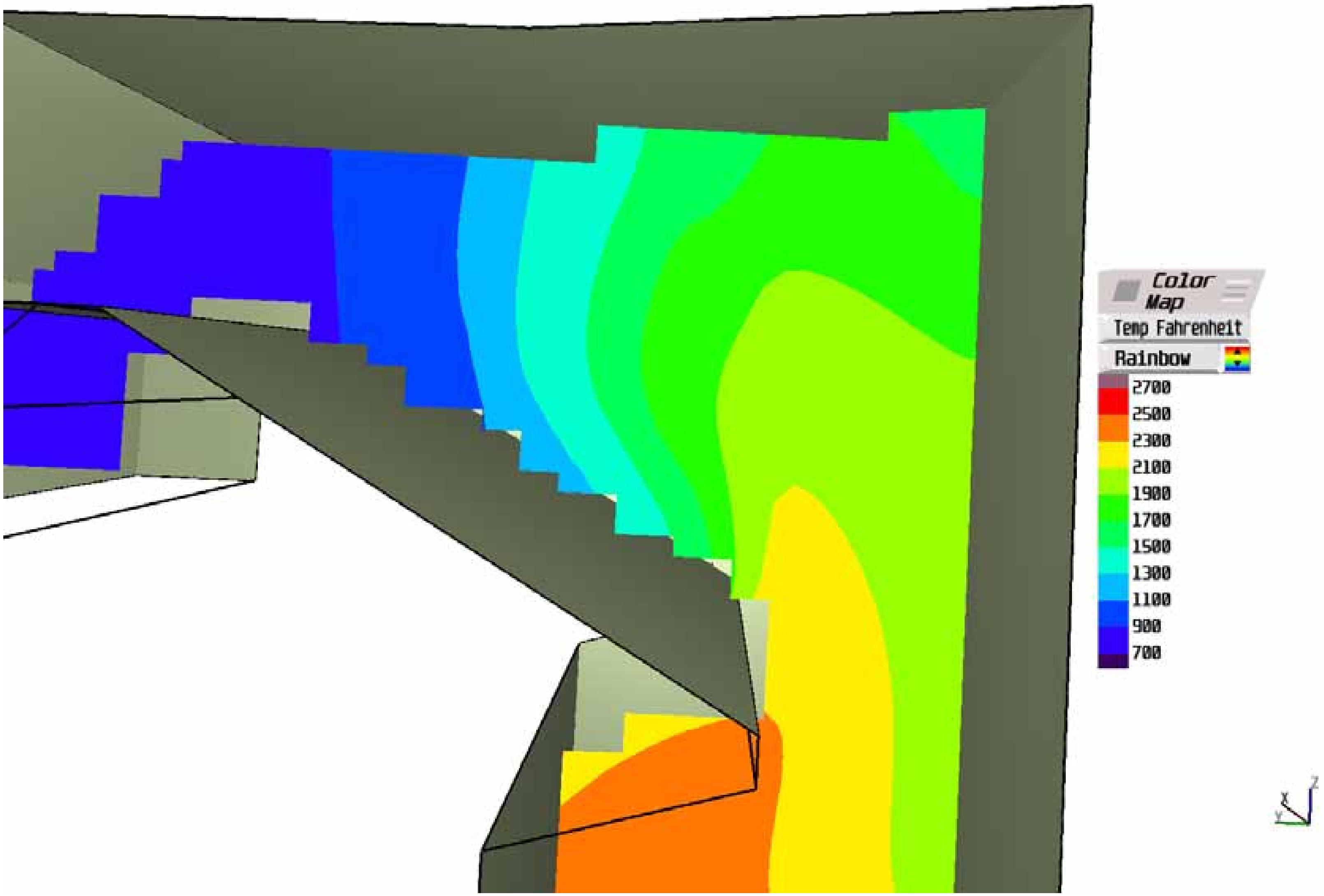


Figure 2. Side-sectional temperature profile in the upper furnace of a 125 MW front-wall coal-fired unit.

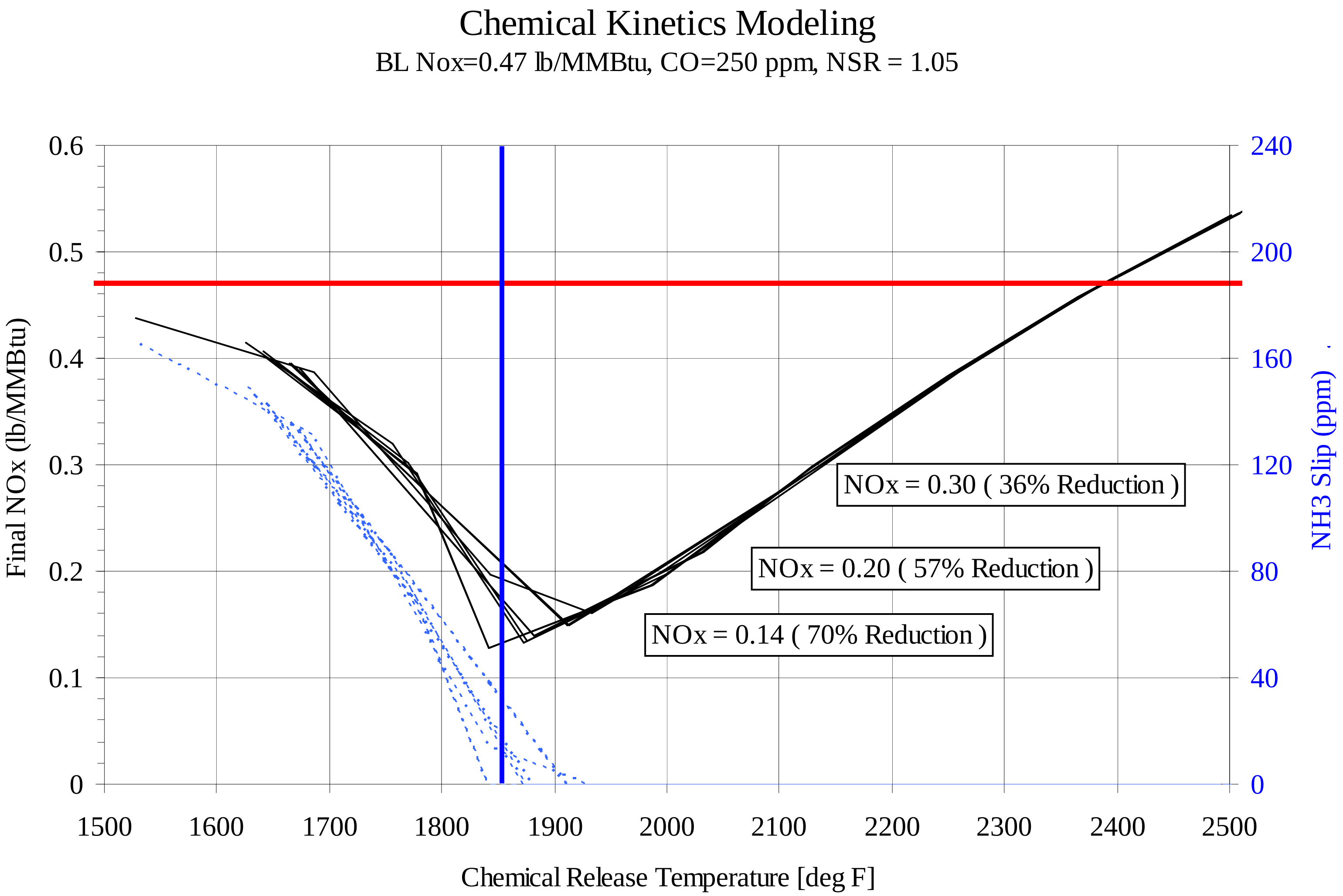


Figure 3. Chemical Kinetics Modeling reveals the potential for SNCR NOx reduction and ammonia slip below 1850 F.

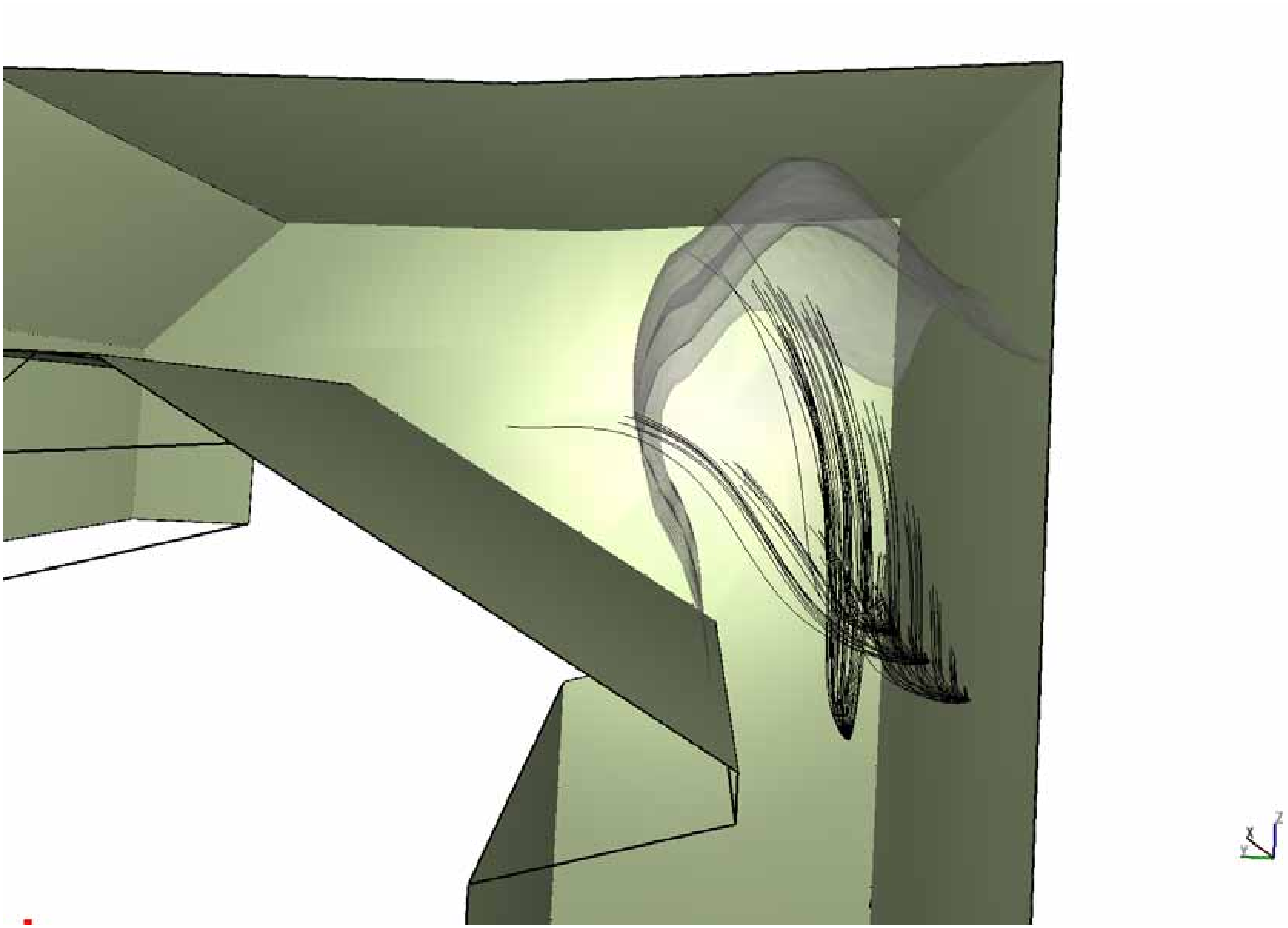


Figure 4. Chemical injection occurs below the low-temperature ammonia-slip-control surface.

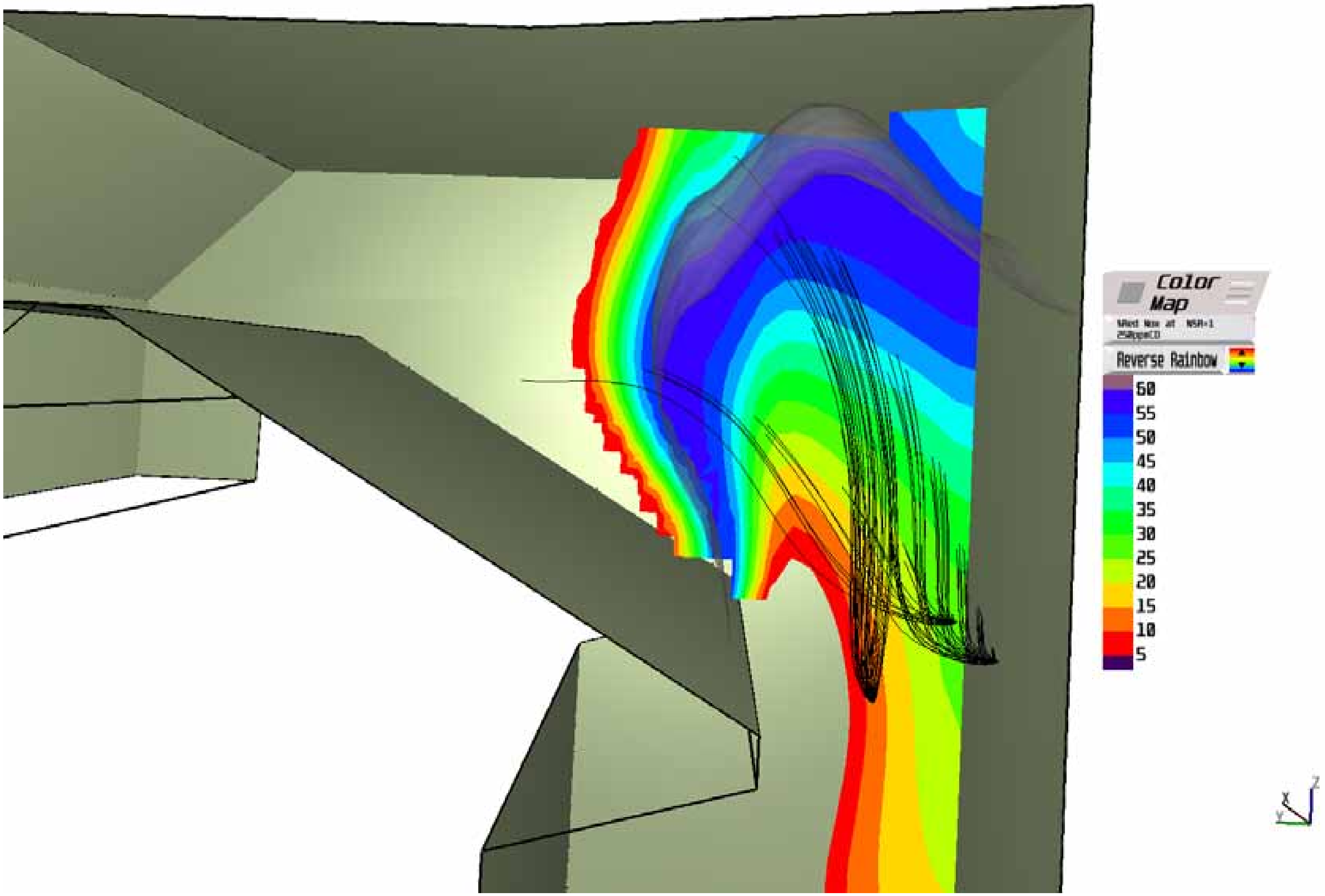


Figure 5. A map of the potential SNCR NOx reduction in the furnace is shown.

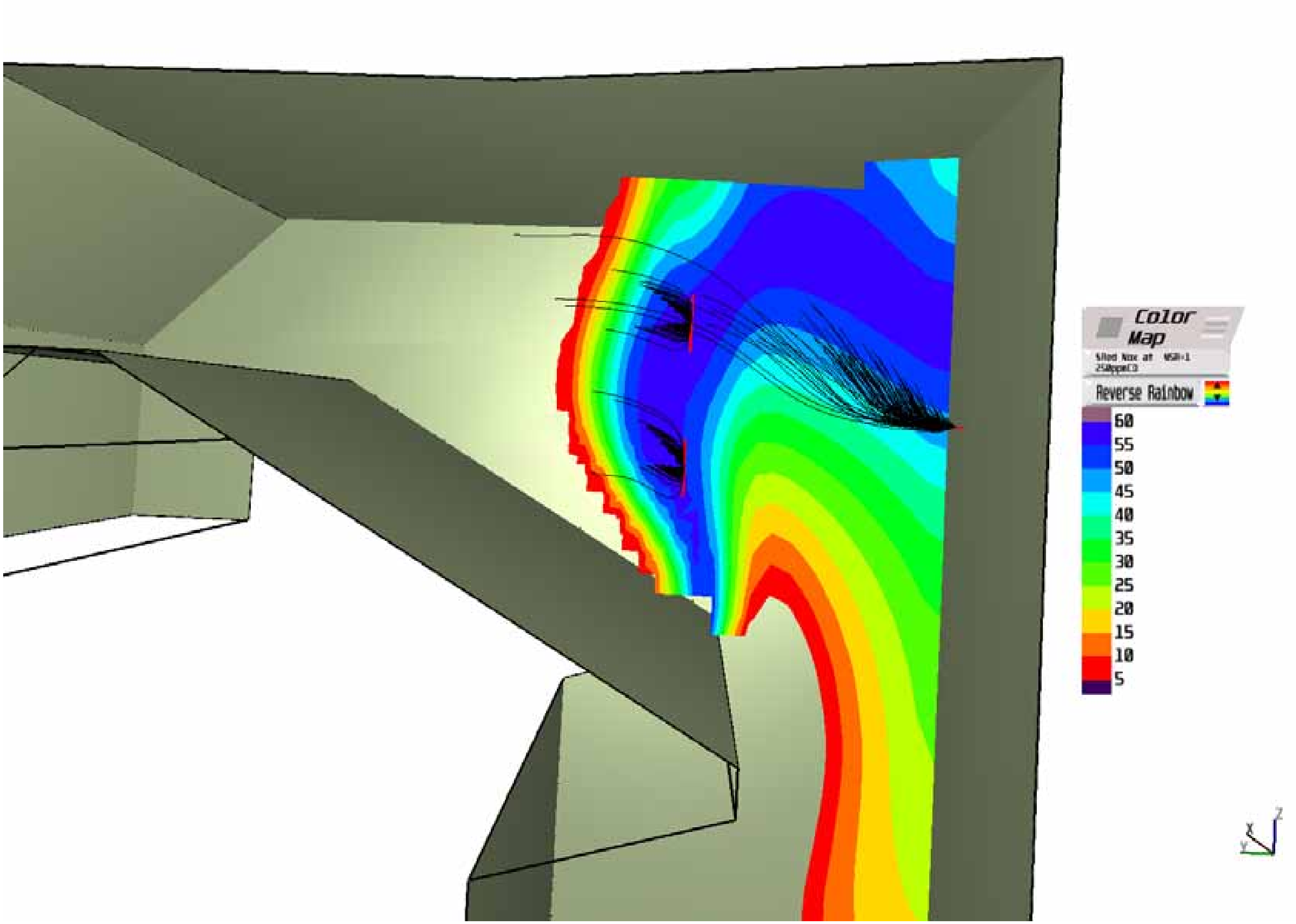
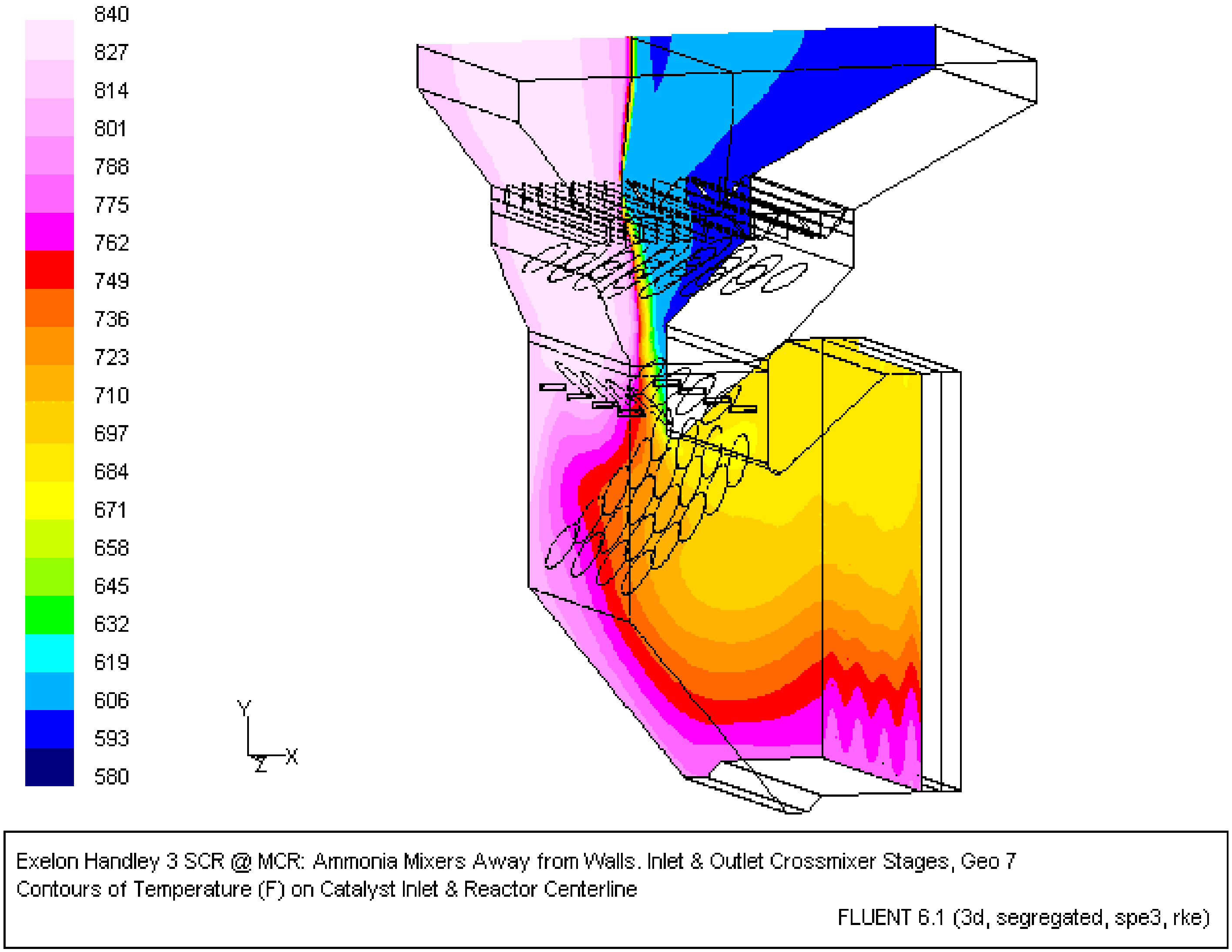


Figure 6. A modified SNCR injection scenario targets maximum NOx reduction.



Exelon Handley 3 SCR @ MCR: Ammonia Mixers Away from Walls. Inlet & Outlet Crossmixer Stages, Geo 7
Contours of Temperature (F) on Catalyst Inlet & Reactor Centerline

FLUENT 6.1 (3d, segregated, spe3, rke)

Figure 7. Vortex mixing plates are used to reduce stratified temperature inlet conditions.

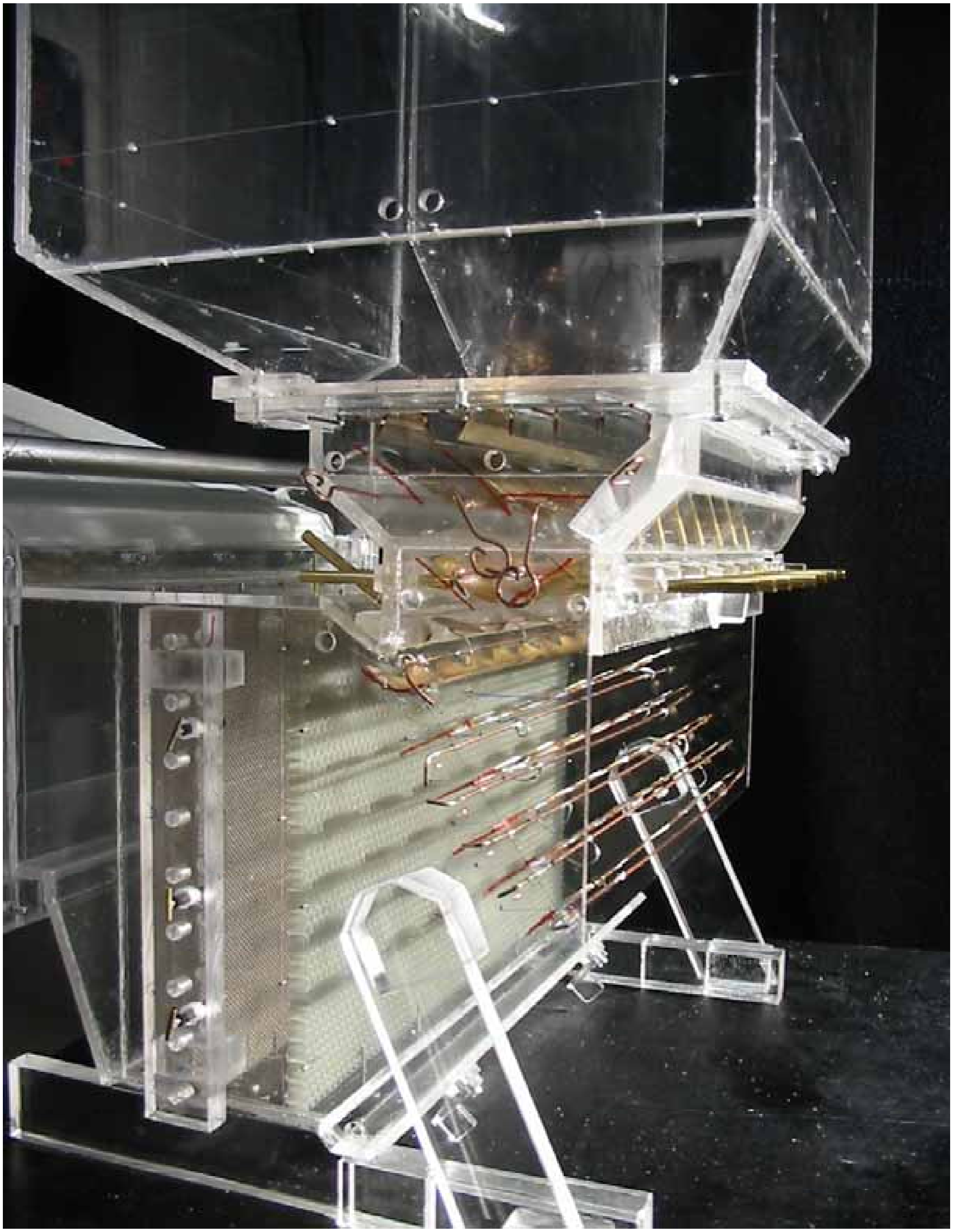


Figure 8. Cold-flow modeling is used to assess the design