



LAYERED REDUCTION TECHNOLOGIES FOR EFFECTIVE NO_x CONTROL

John M. Boyle, Ph.D.
Fuel Tech, Inc., 27601 Bella Vista Pkwy, Warrenville, IL

EXECUTIVE SUMMARY

The control of nitrogen oxides (NO_x) is a well-known requirement for utility and industrial furnaces alike. Although the regulations and corresponding emission limits vary greatly, the need for substantial reduction is becoming universal.

There are a few existing NO_x reduction technologies that have each been proven effective in a variety of applications. Combustion modifications such as low-NO_x burners (LNB), flue gas recirculation (FGR) and staging with over-fire air (OFA) reduce the formation NO_x. Selective non-catalytic reduction (SNCR) and re-burning technologies act to destroy the NO_x in the furnace. Selective catalytic reduction (SCR) utilizes a catalyst bed downstream of the furnace to reduce NO_x. Although each of these technologies has been applied to a variety of applications, they are not all compatible with every furnace condition.

For older units, a reasonable solution to attaining furnace NO_x control may be simply to select the lowest capital cost system and strive for the highest reduction possible until operating costs become the limiting factor. For newer and larger units, the temptation is to select the highest efficiency system and pay the large capital debt over ten or twenty years.

In fact, the most appropriate solution for NO_x reduction on any furnace application is to intelligently apply each of the proven control technologies, as appropriate, to create a layered system. This custom system would logically minimize total cost and minimize risk while achieving the required NO_x control. This more intelligent and agile approach is inherently more adaptable to changing fuels, changing demand for power, steam, or production and a rapidly changing regulatory environment.

This summary will address the intelligent application of each of these technologies. In particular, there are important synergies and interferences that may occur for some applications. The ideal combination of control options may be very different for each furnace needing to achieve compliance.

It is possible that in the next few years, new NO_x reduction technologies may provide the same reliable and proven effectiveness in field. Bio-fuels, Mercury and PM_{2.5} regulations, Green House Gas restrictions will all add to the complexity of the problem. The solution, however, will remain the same; application of a suite of intelligently engineered systems to custom fit regulatory and financial needs.



NO_x CONTROL TECHNOLOGIES

Combustion modifications are considered low-capital, low-operating cost solutions. The term “combustion modifications” is applied to NO_x reduction, but also to unburned carbon, CO emissions, wind-box optimization, coal fineness, furnace slag properties and water wall wastage, among others. The goal of the combustion system is, after all, to provide effective combustion of the fuel. This is not a small point, as many modifications for NO_x reduction can adversely affect combustion.

Combustion Tuning

The first step in providing a well balanced and flexible unit is to insure that the furnace is running within design specifications, or as near as is reasonable. Effective combustion requires tuned fuel preparation and handling (such as mills or feeders), even distribution of the fuel in the furnace, and corresponding distribution of the combustion air.

As furnaces age or when fuel switching has occurred, it is sometimes necessary to reevaluate the design of the air supply and distribution devices. Very often, significant NO_x reduction is achieved with improved combustion and lowered excess air due to relatively simple combustion tuning.

Low-NO_x Burners (LNB)

Low-NO_x burners, see example in Figure 1, are designed to minimize the oxidation of nitrogen while providing effective combustion. NO_x is formed from nitrogen in the fuel and in the combustion air. Thermal NO_x formation, reaction between molecular nitrogen and oxygen in the combustion air, increases exponentially with temperature. Fuel NO_x formation, oxidation of the nitrogen inherent to the fuel, is primarily a function of the excess oxygen at the point of reaction. A third mechanism, Prompt-NO_x, is less significant.

The design of the LNB depends to large extent on the fuel. In general, however, the theory is similar for fuels containing significant nitrogen. An Internal Recirculation Zone is created in front of the burner using proprietary swirl and flow devices. This zone provides rapid heating of the fuel to release volatiles, fuel bound nitrogen, and promote effective combustion in an oxygen-lean environment. The fuel heating rate and secondary air mixing are critical parameters. The lack of excess oxygen limits the NO_x formed from previously fuel-bound nitrogen. The release of nitrogen from the fuel is advantageous in this zone, as any residual fuel-bound nitrogen will likely react in an oxygen-rich environment as combustion completes.

The staging of the combustion air in this near-burner manner also provides a decrease in Thermal-NO_x. As the peak temperature drops in the oxygen-rich portions of the flame, the kinetic tendency to form NO_x falls dramatically.

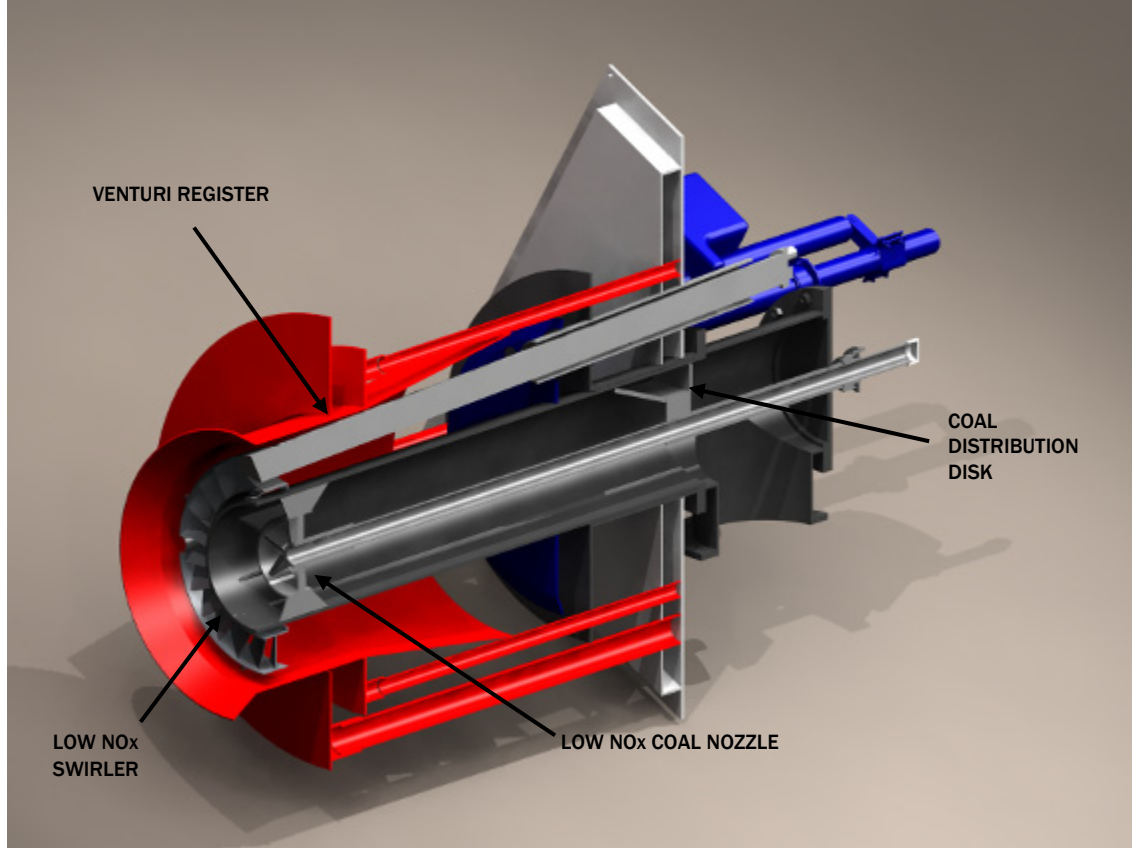


Figure 1 Low NOx Coal Burner

Staging with OFA

Over Fire Air is used to complete combustion when furnace staging is employed for NOx suppression. In this case the burner region of the furnace is operated in a fuel-rich or near stoichiometric condition. This limits the formation of Thermal-NOx and Fuel-NOx by the same mechanisms described above: decreased oxygen availability and lower peak flame temperature. Similarly, Flue gas recirculation, acts to reduce the flame temperature and the resulting Thermal-NOx. This is particularly effective in gas-fired applications.

Furnace staging obviously leads to high CO and a decrease in combustion efficiency, as measured in unburned carbon or non reacted fuel. The role of the OFA is to complete combustion and regain any potentially lost furnace efficiency. Any remaining fuel-bound nitrogen may be oxidized at this point. Effective combustion in the burner zone and sufficient residence time to release the nitrogen are critical to effect staging for NOx control.

An efficient OFA system should be measured on its ability to consume CO and complete combustion. A poorly designed OFA system will diminish the potential for achieving ideal NOx control. Efficient and complete coverage of the furnace gases should be modeled prior to application.

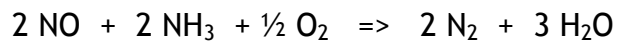
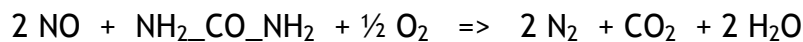


Post combustion NO_x control refers to technologies that cause the reduction of NO after it is formed. “Post-combustion” is not entirely accurate, as the NO_x is formed during combustion and can sometimes be removed before combustion is complete. In each case, the NO_x is reacted with another species, such as ammonia, urea, or natural gas and is reduced to molecular nitrogen. The use of natural gas re-burning has been limited due to the expense and limited availability. In addition, this fuel requires furnace residence time to complete combustion itself.

Selective Non-Catalytic Reduction (SNCR)

The chemical reagent is generally urea (NH₂-CO-NH₂) or ammonia (NH₃). Urea is used in most applications as the aqueous solution is extremely safe and behaves favorably in the furnace. The volatility of urea is less than that of water, and so the droplets themselves can be used as a very effective distribution device for the reagent. Ammonia systems are found primarily in small, low-temperature applications where the chemical distribution is less critical.

The chemical mechanisms are complex, but can be summarized by the following equations:



SNCR is quite simply both selective and non-catalytic. The reactions above are both exothermic, and the products are very stable. The reaction energy, to break down the urea and ammonia molecules prior to NO destruction, comes from the flue gas. This control technology is therefore dependent on flue gas temperature. At very low temperatures, both reagents can lead to residual ammonia slip.

SNCR can be applied both in fuel-rich and oxygen-rich conditions. The fuel-rich chemistry is also very complex, as the combustion reactions are still in progress. Although the chemical utilization is generally lower, the risk of ammonia slip is greatly reduced.

At very high temperatures, the injected nitrogen compounds may be consumed in the combustion process, and may lead to NO formation as described above, particularly in the presence of oxygen. The temperature window for effective oxygen-rich NO_x control is highly dependent on the NO_x baseline and the furnace geometry, but it can loosely be defined as between 1500F and 2300F.

The intelligent application of the SNCR process requires Computational Fluid Dynamic (CFD) and detailed Chemical Kinetics Modeling (CKM).

One application of modeling for SNCR design is shown in Figure 2. The aqueous solution of urea is injected into the upper furnace of a utility furnace. When the water is evaporated, the urea is released and the gas-phase selective reduction begins. This permits the chemical distribution to be tailored to the application through the variation of nozzle design, droplet size and velocity to suit conditions at varied operating loads.

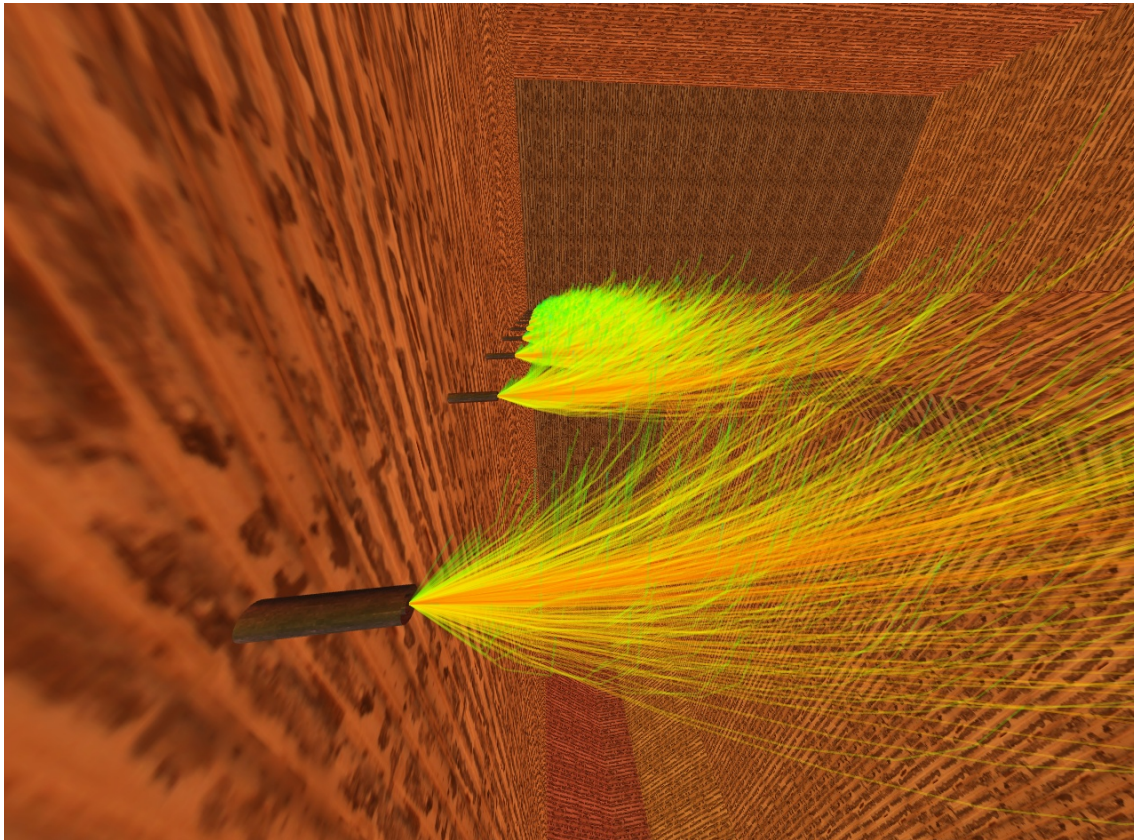


Figure 2 CFD Model of Urea SNCR Injection

A wide variety of injection options must be considered when applying SNCR to a subject furnace. Urea SNCR has been applied to package boilers, cement kilns, stokers, biomass facilities and many utility boilers. Injection technologies include mechanical atomizers, air-assisted injectors, dual-fluid injectors, and multiple nozzle retractable lances.

The risk of ammonia slip can be serious, and must be a prime design criterion in an SNCR system. At low temperatures, where the risk is highest, the effectiveness of SNCR is at its greatest because the competing combustion reactions that may lead to NO_x formation have slowed considerably.

Ammonia slip can lead to the formation of ammonium bisulfate, (NH₄)HSO₄, through reaction with SO₃. It is equally important to understand the SO₃ in the gas stream, as

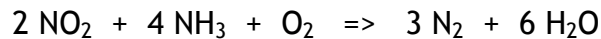
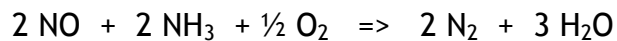


both reactants are required. This can foul downstream equipment operating near 400F, such as an air pre-heater. This risk is controlled through advanced CFD and CKM modeling and by applying conservative optimization strategies at startup.

The intelligent application of SNCR requires experience, a detailed understanding of the subject furnace and a thorough knowledge of the chemistry and urea injection. SNCR systems are low-capital systems with higher operating costs.

Selective Catalytic Reduction (SCR)

The overall reaction chemistry of SCR systems is very similar to that of SNCR:



A catalytic reactor bed is installed downstream of the furnaces, at temperatures generally between 500F and 750F. This reactor promotes the reactions between NH_3 and NO_x with very high efficiency. The primary design factor, the Space Velocity, is a measure of the flue gas volumetric flow relative to the catalyst volume.

Large NO_x reductions (80-95%) are possible, but require correspondingly large reactors. The distribution of the ammonia and NO_x at the catalyst inlet are very important for effective treatment. SCR catalysts also promote the oxidation of SO_2 to SO_3 , which can lead to ammonium bisulfate formation in the presence of excessive ammonia slip. Large SCR systems are very high capital cost but operate more efficiently than SNCR systems.

Smaller SCR reactors are generally 30% of full-size installations and are designed to provide moderate stand-alone NO_x reductions of between 30-60%. Similar to the large applications, the performance of these smaller SCR applications is dependent on the NO_x baseline and achievable distribution of ammonia and NO_x .

Previous applications of this technology have used residual ammonia from an upstream SNCR process as the feedstock. They generally have not used the SCR reactor to maximum benefit, although the synergistic effects on the SNCR process were significant.



SYNERGIES AND INTERFERENCES IN THE LAYERED APPROACH

A layered approach to NO_x control is the natural solution for most applications. Each of the technologies discussed has both strengths and weaknesses. It is difficult to ignore the low-capital low-operating cost benefits of combustion modifications such as Low-NO_x burners. In fact, lowering the apparent baseline NO_x emissions to downstream control measures reduces risk and cost. Although this one synergy may be obvious, others are less apparent but equally intelligent.

The approach to designing a layered system begins in the fuel supply and extends to the stack. Combustion tuning and fuel switching should be evaluated to harvest this low-hanging fruit. These efforts will generally lead to improved furnace efficiency through decreased CO and LOI, improved facility operation and availability.

In addition, combustion tuning provides a lower NO_x formation rate through decreased excess air. Combustion modifications are highly specific to the application, the fuel and the process. Although wall-fired utility boilers clearly benefit from LNBS, even stoker units can see improved emission rates and efficiencies with air balancing.

A well-tuned furnace provides the ideal application for post-combustion NO_x control. SNCR systems are very flexible and capable of targeting the ideal temperature window for NO_x reduction with minimum ammonia slip across the load range. Consistent furnace operations and good CO burnout provide an ideal environment for SNCR reduction.

Ideal SNCR system performance is separate from but dependent on the combustion conditions. Intelligent application of LNB and furnace staging with OFA requires a conservative approach that allows the SNCR system and the furnace to operate effectively. Potential interferences with the SNCR system, such as high CO or insufficient residence time, are also drains on furnace efficiency.

The SNCR process can operate effectively in both fuel-rich and fuel-lean environments. In this case, furnace staging leads not only to decreased NO_x formation, but also to an opportunity for further SNCR NO_x reduction.

As discussed earlier, SNCR reduction can also be limited by ammonia slip concerns, especially for high sulfur fuels. This is evident in many field applications where the system is methodically tuned to avoid ammonia slip. Conversely, in low sulfur applications where ammonia slip constraints are not significant, NO_x reduction efficiencies can be dramatically higher.

In a similar manner, the presence of a downstream SCR catalyst can provide a sink for ammonia slip before it is able to interact with SO₃. This has been the basis for hybrid SNCR/SCR systems. In addition, the use of a small SCR reactor, rather than a large reactor, dramatically decreases the catalytic oxidation of SO₂ to SO₃, which can otherwise be significant.



The use of a small SCR reactor can provide significant NOx reduction. In fact, the combustion and SNCR control measures provide a lower apparent baseline to the catalyst reactor, which provides even greater reduction as a result, Figure 3. This powerful effect is due to the ammonia slip constraint placed on the SCR design. As the baseline NOx decreases, the residual ammonia becomes a proportionately smaller amount, providing further removal capability.

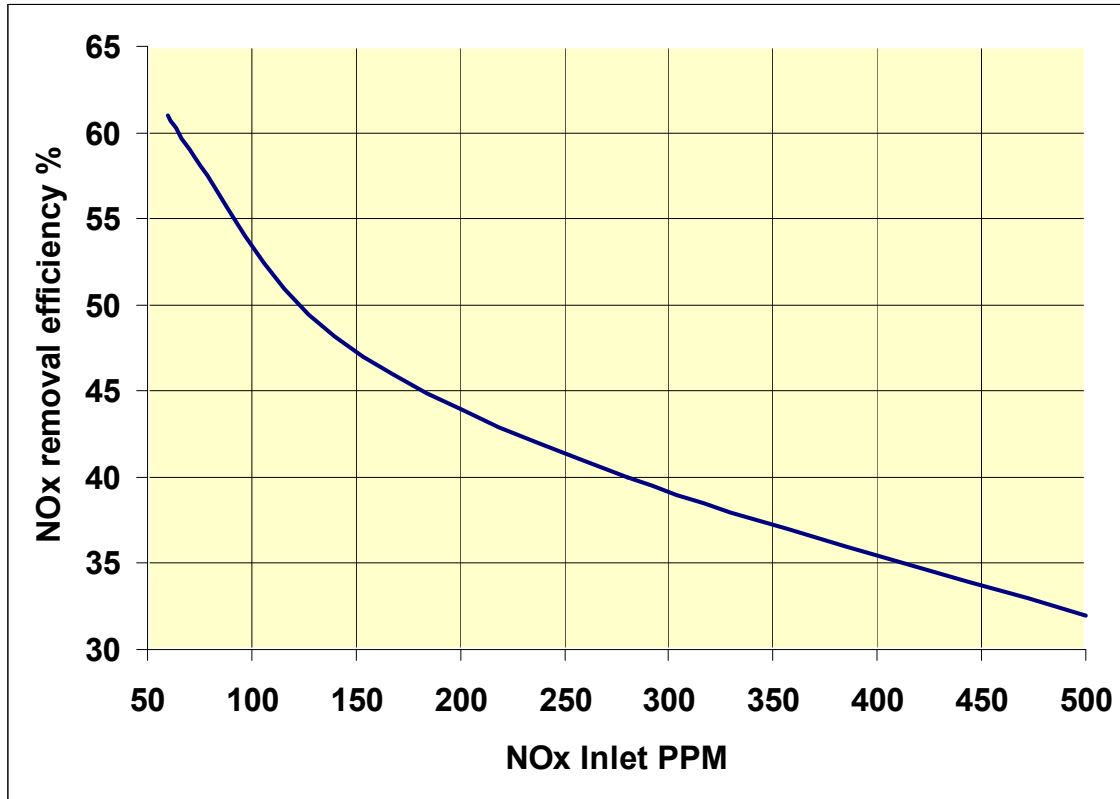


Figure 3 SCR Performance Improves as Baseline NOx Decreases

The intelligent application of SCR, as shown in Figure 4, utilizes the most advanced SCR design criteria and tools. Physical flow and CFD models are used to create the ideal velocity and species distributions, without the need for a separate reactor facility. This can be accomplished with significantly less capital.

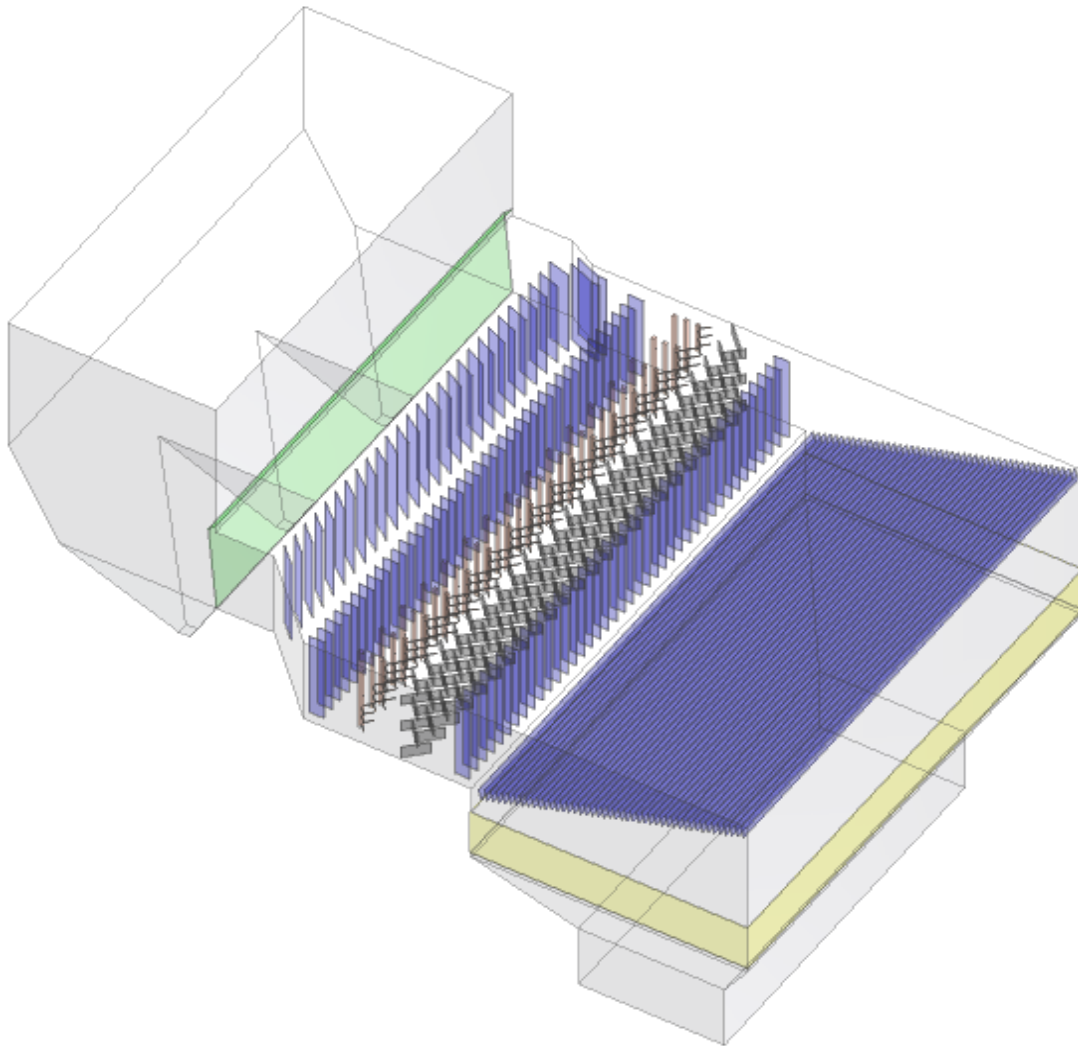


Figure 4 Advanced SCR Reactor

Advanced SCR

The Advanced SCR concept of layered technologies is an intelligent approach to a full suite of the best commercially available solutions. A full scale SCR can be designed to achieve 80% NO_x reduction. An advanced SCR provides this same reduction at half the cost of the stand alone system and with greater flexibility, greater customization and tolerance for fuel and load changes.