

# Chapter 8

## Back End NOx Controls

### Editor's Note:

Chapter 8 – Back End NOx Controls – This section was written by Chuck Solt and is updated from material in the NOx Emissions course presented by Rutgers University until 2007

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# NO<sub>x</sub> REMOVAL TECHNOLOGIES

If NO<sub>x</sub> cannot be prevented sufficiently in the combustion process, the only alternative is to remove it from the exhaust stream. NO<sub>x</sub> removal technologies have been developed as early as the mid-1950s, and in common use since the mid 1980s. Some of these technologies have gained wide acceptance, while others are just emerging.

The Existing Technologies include:

- SNCR - Selective Non-catalytic Reduction
- NSCR - Non-selective Catalytic Reduction
- NO<sub>x</sub>Out
- SCR - Selective Catalytic Reduction

Emerging Technologies (some of which may never emerge)

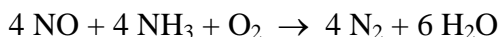
- RAPER-NO<sub>x</sub>
- SCONOX
- LoTO<sub>x</sub>
- Activated Carbon Absorption

We will look at each of these technologies individually, first at the technologies that have wide usage and then at the emerging technologies.

## EXISTING TECHNOLOGIES

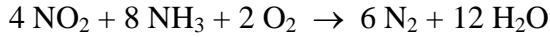
As previously discussed, NO<sub>x</sub> emissions consist of both NO and NO<sub>2</sub>. Accordingly, the NO<sub>x</sub> control technology must address the NO<sub>x</sub> compound emitted by the source, or if (as in most cases), the source emits both, it must either react both compounds or convert one into the other before reacting the second compound into N<sub>2</sub> and water. Several of the existing technologies we will discuss are based on the following reaction:

For NO removal:



or

For NO<sub>2</sub> removal:



This reaction is called “selective reduction” because it uses a reagent to react with the NO<sub>x</sub>.

### **Selective Non-catalytic Reduction (SNCR).**

In this type of process, a reactant is sprayed into the exhaust stream. Under the right temperature conditions, the NO<sub>x</sub> will react with the reactant, eliminating the NO<sub>x</sub> without producing other regulated pollutants. The first of these technologies was *Thermal DeNO<sub>x</sub>*. It was developed by Exxon in about 1956. In This technology, ammonia is sprayed into the post-combustion area of a boiler or furnace when the temperature is 1650 °F. Under these condition, a 50% reduction of NO<sub>x</sub> can be achieved. The reaction is temperature sensitive, and the window is small. If the temperature is to high, ammonia will convert to NO<sub>x</sub> faster than the reduction process. If the temperature is to low, the reaction with the NO<sub>x</sub> will not occur.

Fuel Tech Inc. of Stamford CT did development work on the basic concept through part of the 1970 and 1980 and commercialized a technology they called NO<sub>x</sub>OUT. While this technology is still SNCR (like Thermal DeNO<sub>x</sub>, it uses no catalyst), the primary difference is that the NO<sub>x</sub>OUT process uses urea as a reactant instead of ammonia. The urea gives the technology a broader and slightly lower temperature window. Also, urea can be transported and stored as a solid.

With the exception of the better temperature window, NO<sub>x</sub>OUT still had most of the same application limitations, but during the retrofit requirements imposed by the RACT requirements in the Clean Air Act Amendments of 1990, many existing boilers were retrofitted with NO<sub>x</sub>OUT. It is still the technology of choice in some boiler applications.

### **Selective Catalytic Reduction (SCR)**

#### *Principle*

Catalyst can be used to make the same chemical reaction occur in different temperature ranges. In the early 1980s, Germany developed SCR for use on coal fired power plants, and in Japan, it was applied to gas turbines in the mid-1980s. In the late 1980s, the South Coast Air Quality Management District (regulating the LA basin) developed rules and guidelines for gas turbines based on the availability of SCR.

The chemical reactions are the same as SNCR, but the reactions are catalytically driven. The temperature range depends on the catalyst used:

### Alternative Systems

- Conventional SCR Systems are called base metal systems. They usually use a Vanadium Pentoxide catalyst. The best performance will be in the range of 650° to 750°F.
- For low temperature applications, Precious Metal is used, usually platinum. These systems can be used at temperatures as low as 350°F, and as high as 550°F.
- High Temperature applications usually use Zeolite catalysts and have been used successfully at temperatures as high as 1050°F.

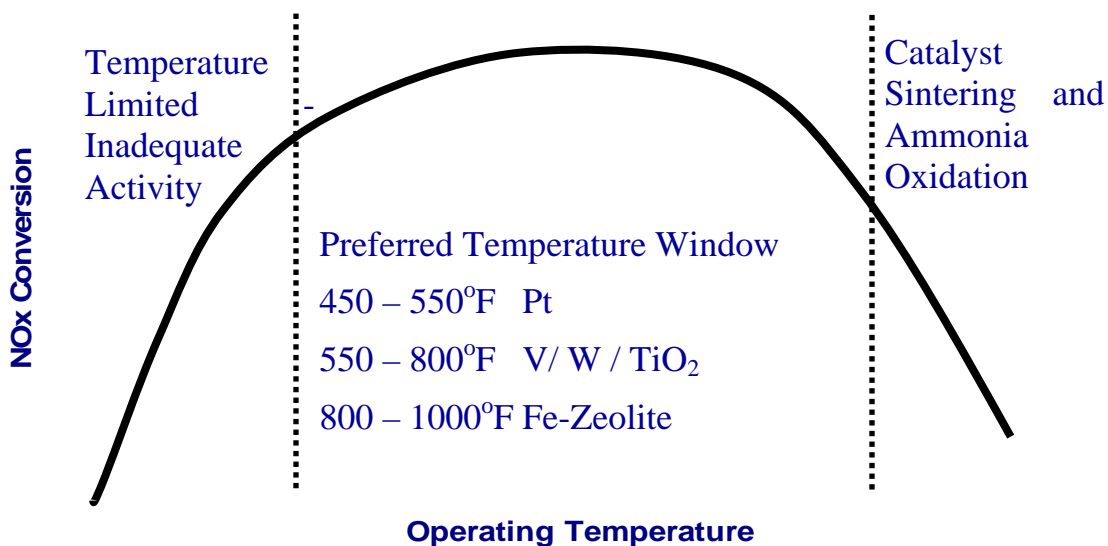


Figure 8- 1. SCR Temperature vs. Catalyst Activity

### NOx Reduction vs. Ammonia Slip

As can be seen in the chemical reactions shown above, in a system emitting primarily NO, the reaction ration of NOx to ammonia will be nearly 1:1. If less ammonia is injected, some of the NOx will go unreacted and pass into the atmosphere. If a higher ratio is used, some of the ammonia will go unreacted and pass into the atmosphere. This unreacted ammonia is called *ammonia slip*. The NOx removal effectivity is a function of the amount of catalyst used and the ammonia/NOx ratio. If the ratio is stoicometric (exactly the correct ration to react all of the NOx and ammonia), there will be some NOx emissions and some ammonia slip. The longer the catalyst path, the more NOx molecules will find ammonia and react on the catalyst surface. So, the effectivity of the system has a tradeoff. The permit can sacrifice ammonia slip to achieve better NOx reduction, or visa versa, and both can be improved by sacrificing size and cost of the system.

Most permits today require NO<sub>x</sub> in the range of 2 to 3.5 ppm (at 15% O<sub>2</sub>, dry) and Ammonia slip of 6 to 10 ppm. Even at 10 ppm, catalyst life is definitely impacted, but ammonia has been recognized by the US EPA as an adverse environmental impact that should be considered in a BACT determination. Unfortunately, the EPA stopped short of recommending a means of making the determination, so the permitting agency usually selects the lower NO<sub>x</sub> level and determines the ammonia slip on an economic basis.

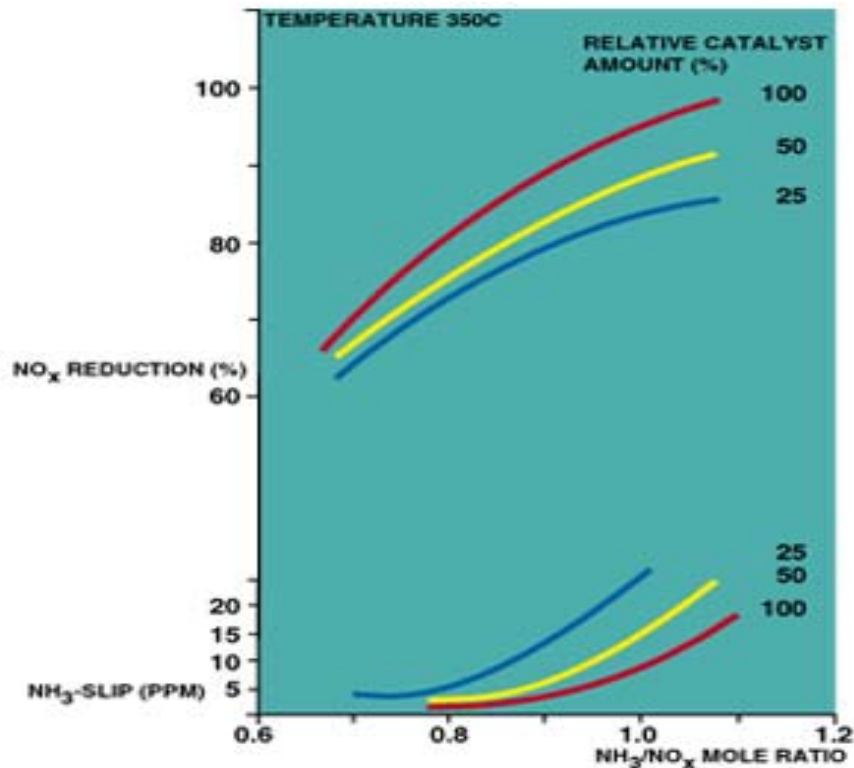


Figure 8-2. Ammonia Feed Effects on Emissions

### Catalyst Performance Over Time

All catalysts become deactivated with time due to a number of operating factors, including:

- Sintering: Pores are blocked and fused at High temperatures
- Poisoning: Foreign Molecules Bind to the Catalyst
- Pore Blockage: Fine Particles Become Imbedded in the Pores

Most SCR systems install the catalyst in 2 or more beds or layers. These can be replaced individually. Figure 1.3 is an example of a catalyst replacement scenario. In the system depicted, the system was initially installed with two catalyst beds, but space to add a third bed. If initial performance did not meet permit requirements, the third bed



could have been installed immediately to improve performance. If the system met initial performance, the plan calls for addition of the third bed at the end of the second year operation, when NOx and ammonia levels were both projected to reach the permitted level. In subsequent years, one of the catalyst beds would be replaced as the NOx or ammonia level reached the permit level.

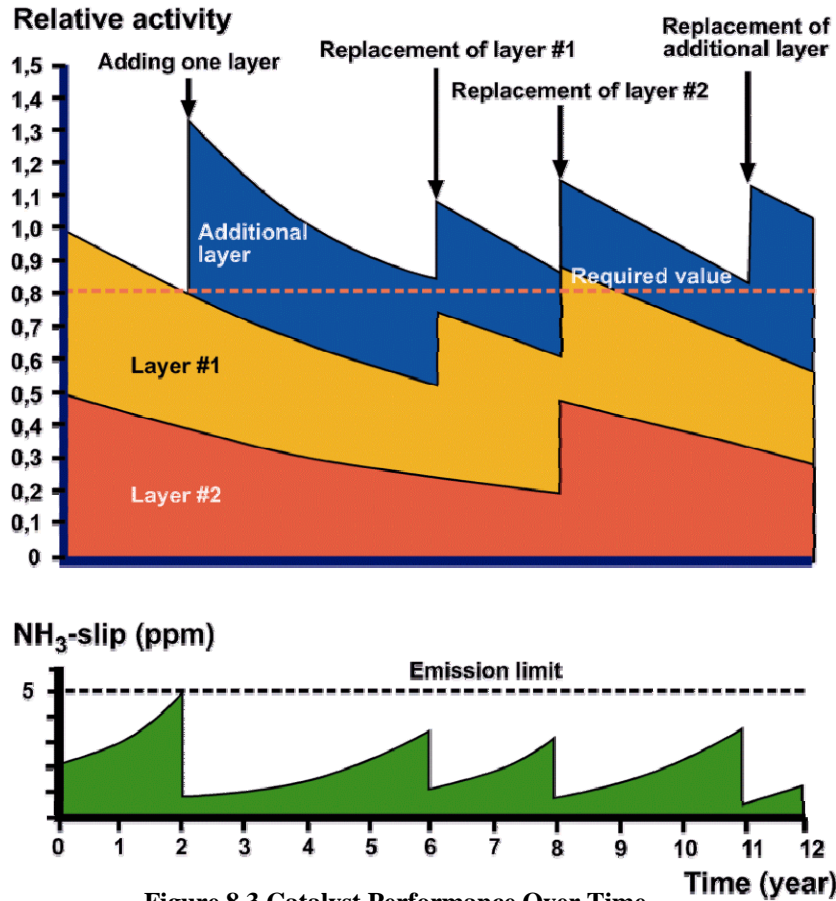


Figure 8.3 Catalyst Performance Over Time

### Early Application of SCR

The first applications of SCR were in coal fired generating plants in Germany, followed shortly thereafter by Gas turbines in Japan. In the mid 1980s, the South Coast AQMD (LA Basin) made a BACT determination that SCR performance should be the permit basis for several gas turbine permits. This determination was based primarily on the Japanese experience. At that time, the permitted levels were based on water injected turbines operating at 42 ppm and SCR at guaranteed effectivity of 80% for a permit level of 9 ppm (15% O<sub>2</sub>, dry).

By the late 1990s, permits for gas turbines were based on lean-premix combustion at 25 ppm and SCR effectivity of 90% for a permit level of 2.5 ppmvd.

## Reagent Alternatives

So far, we have been limiting our discussion of reagents to ammonia, but in fact, ammonia can be used in different forms, and there are other chemical reagents that will also reduce NO<sub>x</sub> into nitrogen and water. We mentioned urea in the discussion of NO<sub>x</sub>Out, but urea can also be used in SCR, in different forms. Each of these reagents has its own advantages and disadvantages. The most commonly used reagents are anhydrous, ammonia, aqueous ammonia and urea.

### Anhydrous Ammonia (liquefied ammonia without water)

Good qualities:

- The cost of the ammonia and the ammonia storage and handling system make this the most economic alternative.
- The volume of the reagent is small, saving on transport, storage and handling.
- It is easy to vaporize, reducing the complexity, cost and maintenance of the reagent handling system.

Bad qualities:

- Ammonia is regulated as a toxic substance 36 states.
- Storage of the quantities of ammonia required for SCR will trigger the requirement for Risk Management Planning.
- Ammonia slip is a precursor to PM<sub>2.5</sub>.

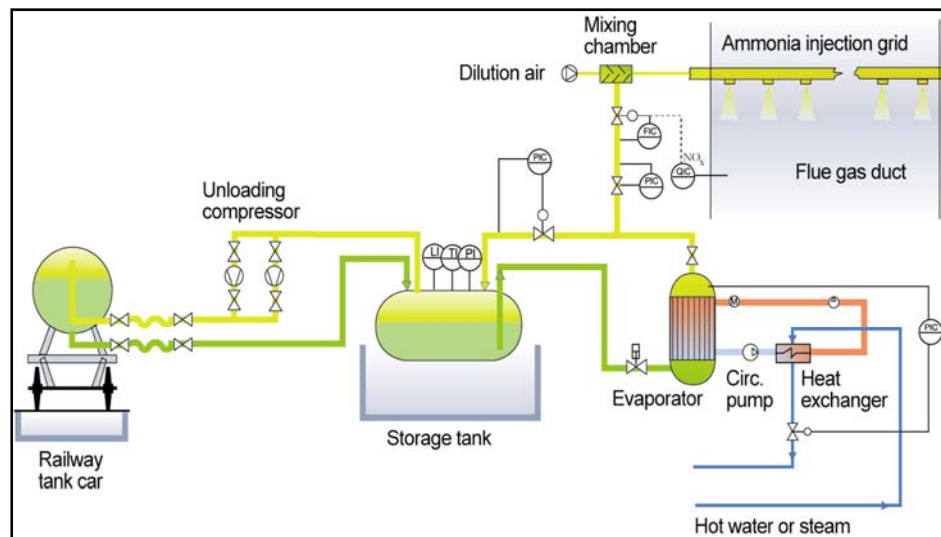


Figure 8-4. Anhydrous Ammonia Flow Diagram

In the anhydrous ammonia system shown in figure 8-4, the ammonia is delivered by rail car, and transferred to an on-site storage tank. It is then sent to an evaporator where process heat is used to vaporize the liquid before it is mixed with dilution air and injected into the exhaust stream.

**Aqueous Ammonia** (ammonia absorbed into water)

Good Qualities:

- Perceived as low Toxic Risk

Bad Qualities:

- The mass and volume of reagent to be transported, stored and handled is far greater.
- The capital and operating costs are both higher.
- Far more process heat is required to vaporize the water/ammonia solution.
- Ammonia Slip is the same the same as with anhydrous ammonia.

**Urea** (in most systems, the urea is converted to ammonia as it is needed)

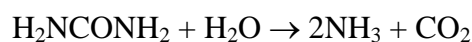
Good Qualities:

- It can be shipped and stored as a solid.
- The toxic and hazard risk is much lower since ammonia is not transported or stored in significant quantities.

Bad Qualities:

- This is the most costly system on both a first cost and operating cost basis.
- The handling system for the solid urea is far more complex and requires more maintenance.
- The Urea-to-ammonia processing facility is costly, complex and requires more energy.
- Ammonia slip is the same.

The urea to ammonia system shown in figure 1.5 dissolves the solid urea into water. The solution is evaporated and passed through a decomposition catalyst where the urea is converted into ammonia.



There are no pressure vessels to pose a risk of hazardous or toxic release.

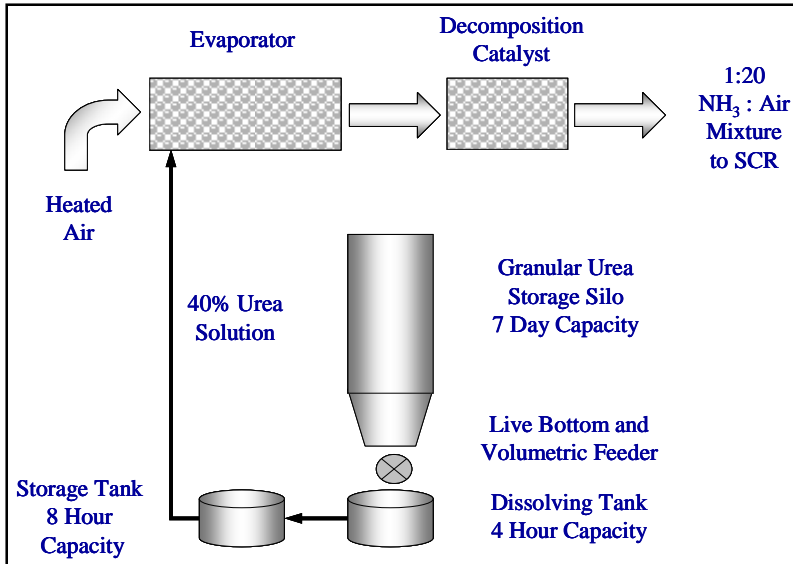
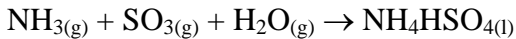


Figure 8-5. Urea to Ammonia "On Demand" System

### Ammonium Bisulfate Formation

A potential problem which must be addressed in the application of SCR is the potential formation of Ammonium Bisulfate. Some of the catalysts used in SCR will oxidize SO<sub>2</sub> into SO<sub>3</sub>. A CO oxidizing catalyst will do the same. If there is excess ammonia, it will react with the SO<sub>3</sub> to form Ammonium Bisulfate.



The bisulfate will deposit in the cold end of the boiler and economizer and plug the spaces between the heat exchanger fins. This chokes off the air flow and reduces the effectiveness of the heat recovery.

There are several design consideration that will minimize the risk, including:

- Designing the system for low ammonia slip,
- Designing the catalyst for low SO<sub>2</sub> to SO<sub>3</sub> oxidation
- Installing an economizer bypass system and/or
- Installing an air heater to assure that the temperature in the cold end does not drop to the point where the bisulfate will precipitate.

Most or all of these design considerations will have air permit considerations.

## Gas Turbine Applications

Because of the temperature windows associated with SCR, the system is usually installed in the heat recovery steam generator (HRSG). The system selected will be dependent of the HRSG.

- **New HRSG** – If the application is a new cogeneration system, the HRSG will be designed to accommodate the SCR. Usually the evaporator section will be split, and the SCR will be located between the evaporator sections where the temperature range will allow the use of a base metal catalyst system. These system are commonly permitted at 3.5 ppm or less.
- **Retrofit Existing Cogeneration** – In an existing system, it is usually impossible to split the evaporator section of the HRSG. In this case, a base metal system can not be used because the temperature before the evaporator is usually to high, and after is to low. The most common option is to locate the SCR between the evaporator and the economizer. The temperature range in this area will accommodate a precious metal SCR system. These system can also achieve 3.5 ppm or less.
- **Peaking Generator** – In a peaking generation application or any other application where there is no heat recovery, the only alternative is usually a zeolite catalyst system. Experience on these system is more limited. The first system was a demonstration project with limited success. The second system, consisting of 4 gas turbine 5000 HP natural gas compression units, permitted at 8 ppm for operation in California. The initial SCR system failed in that it had numerous exceedences. At the insistence of EPA Region IX, the operator installed a second SCR system from a different supplier. That system has been operating successfully at less than 8 ppm for about 4,000 hours per year each since installation (about 2000). Several other units have been installed on 25 MW peaking turbines in California, permitted at 5 ppm. These have not had consistent results, and, since they are peakers, they do not accumulate many hours of operation. In making a BACT/LAER determination, at the time this was written, 8 ppm can clearly be justified, but 5 ppm is marginal and although suppliers may guarantee as low as 2.5 ppm, there is not operating experience to support a permit at this level.

### Considerations

When applying SCR to a gas turbine application there are several design constraints that must be considered:

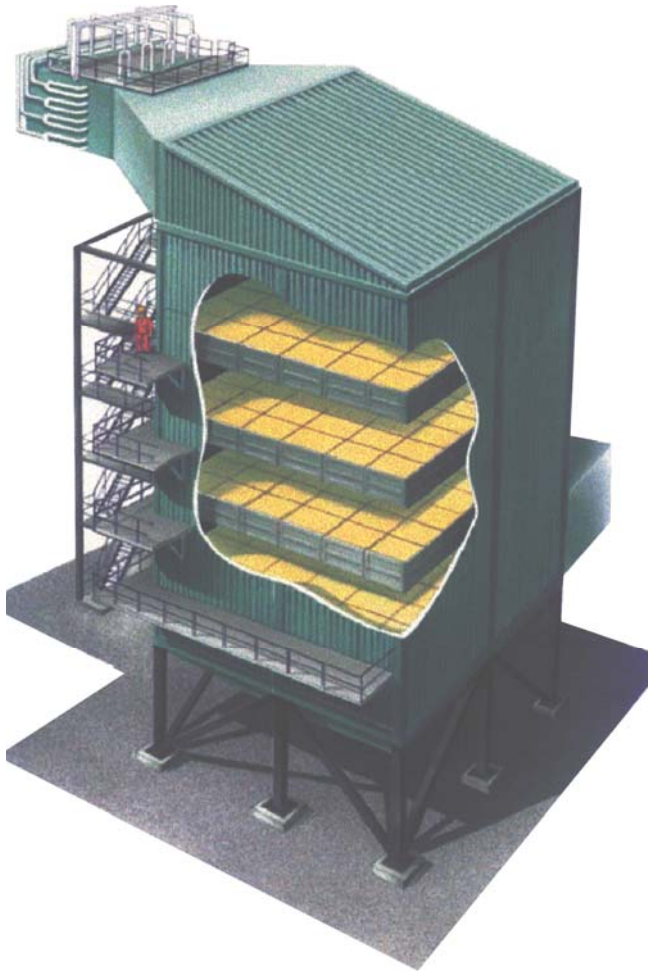
- **Turndown** – As the load on the gas turbine decreases, the exhaust temperature will also decrease. The decreasing temperature in the SCR will affect its performance. I is important to assure that the temperature will support the effectivity necessary to meet NOx limits throughout the design load range.

- Duct Burners – Gas turbine exhaust still contains about 13 to 16% oxygen, enough to support the combustion of a lot more fuel. In many cogeneration applications, a “duct burner” will be inserted into the exhaust. This can be used to increase the temperature of the exhaust from 900 to as much as 2300 Deg. F. The temperature variation in the SCR resulting from the duct burner must also be considered to assure compliant operation over the duct burner range, as well as the gas turbine turndown.

## Boilers and Heaters Application

There are also configuration considerations for boiler or heater applications. These include:

- The SCR catalyst must be located in the boiler at a point where it will see the necessary temperature range.
- Since these systems can be very large (often over 30 feet high) serviceability is a major consideration. The catalytic panels will have to be replaced periodically, and this will require the access, space and handling capability to remove and replace the panels.
- For boilers burning coal or residual oil, ash is a consideration. The SCR catalyst panels can be located before or after the ESP, scrubber or bag house. If it is before, the catalyst must have very large passages and will usually be configured to have the exhaust flow going downward through the catalyst. This will allow the ash to pass through the catalyst panels without building up and blocking air flow. The alternative is to put the SCR catalyst after the cleanup systems. In that case, ash is not a problem. The catalyst can have very small passages, keeping the size and cost of the system down, but temperature is now a consideration. In some applications it is necessary to reheat the exhaust to achieve the correct temperature for the SCR.
- Turndown is also a consideration for boiler applications, much as it is for gas turbines (see above).
- SO<sub>2</sub> to SO<sub>3</sub> oxidation is a concern because of the ammonium bisulfate formation, mentioned above. It is important to inject the ammonia in a region where the temperature will not drive that oxidation.



**Figure 8-6. Typical SCR Configuration for a Large Boiler**

If the SCR is installed after the exhaust clean-up systems, there are different considerations. On the positive side:

- Dust loading is very low.
- The catalyst passages (pitch) can be much smaller. This will reduce the size and cost of the reactor.
- Catalyst life will be long.

On the negative side:

- It is often necessary to have a heat exchanger or burner after the ESP or baghouse to get the temperature over 570°F.



## **Reciprocating IC Engine Applications**

There are several limiting characteristics in applying exhaust clean-up systems to IC engines. First is the cycle. If the engine is compression ignition (a diesel engine), there are relatively few systems currently in service. There are some new systems in the late stages of development involve the use of “NOx traps” for particulate matter, but the on-line regeneration systems required have not yet been adequately demonstrated. The low experience level of emission control systems has not been much of a problem until recently because diesel engines are usually used for emergency service or portable equipment and have not required permits.

The other IC engine cycle is spark ignition. This is the same principle as a gasoline fueled automobile engine. It is also the most common cycle for stationary engines burning natural gas. The first consideration in choosing an exhaust gas clean-up system for an IC engine is whether the engine is “Rich Burn” or “Lean Burn”.

A rich burn engine will have very little or no oxygen in the exhaust stream. As noted Chapter 6, NSCR systems can be used only when there is no oxygen. Accordingly, for lean-burn engines, the exhaust cleanup system of choice would be the NSCR or three-way catalyst system. There is no reducing agent required, and the system is very inexpensive, both first costs and operating cost. These systems will, however, require the use of a fuel to air ratio controller and an oxygen sensor to assure that the oxygen in the exhaust is kept near zero.

A lean burn engine will typically have 7% oxygen in the exhaust. Accordingly, NSCR will not reduce the NOx, and an SCR system must be used. This will require the transport, storage and handling of the reducing agent and the system will be both complex and costly to own and operate.

## **New Emission Control Technology for Lean-burn IC engines**

At least two companies are now marketing a new system that allows the use of a simple inexpensive NSCR emission control system on lean-burn engines.

These systems use exhaust gas recirculation to reduce the oxygen in the exhaust to near zero. The engine performance is that of a lean-burn engine, but with no oxygen in the exhaust, an NSCR system can be used. This allows the superior performance of a lean-burn engine and the simplicity and low cost of NSCR. A portion of the exhaust is diverted thru a cooler and regulating valve and then is mixed with the incoming air. The amount of exhaust recirculation is controlled to keep the oxygen at the NSCR system at zero.

Attainment Technologies of New Iberia LA currently has 23 engines in the 1200 HP range. The high time engines are currently over 12,000 hours, meeting guaranteed NOx emissions of less than 20 ppmvd (15% O<sub>2</sub>).



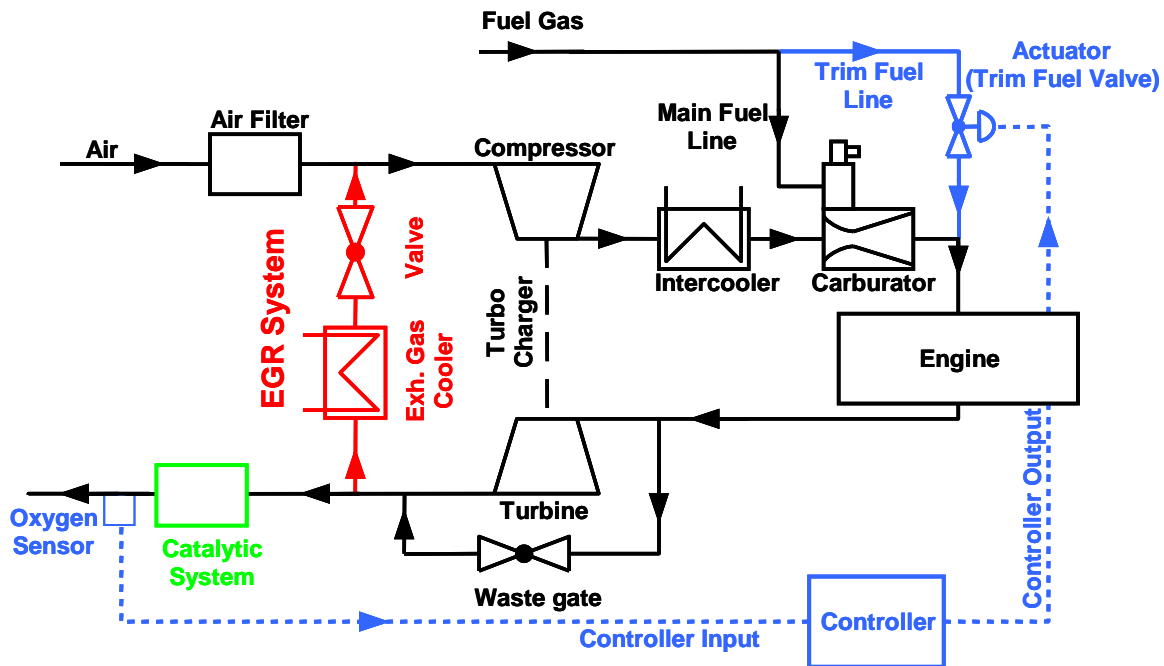


Figure 1.6 Attainment Technologies EMU 1001 Virtual Lean Burn Combustion Process.

Bluepoint Energy of El Dorado Hills, CA also has several generator sets operating with a similar system and producing similar results.

## SCR Summary

### Process Design Issues

- NO<sub>x</sub> Removal Efficiency (impacts costs and ammonia slip)
- Ammonia Slip (Consideration of catalyst life vs. ammonia slip)
- SO<sub>2</sub> Oxidation to SO<sub>3</sub>
- System Draft Loss (imposing backpressure on the combustion device)
- Catalyst Life Expectancy
- Ammonium Bisulfate Formation
- Application Specific Issues

### Considerations

- Little process impact
- No design impact on combustion source
- Proven Technology
- Well Supported
- Permitting impacts

- RMP
- Ammonia Slip
- Real-estate
- Profile

### **SCR Experience**

- 80 to 90% reduction have been achieved with up to 20 years of operation.
- Can be combined with SNCR for lower emissions. No experience noted.
- Catalyst lifetimes generally good, but impacted by low ammonia slip limits
- Widely applicable to many types of sources
- Low technical and economic risk
- SCR is a mature technology
- Often, many real cost factors are not identified and considered when permitting and budgeting.

## EMERGING TECHNOLOGIES

Over the last 10 years, a number of new technologies have been shown to have potential. This section reviews several of them. It is not necessarily a complete list, and some of these technologies have achieved more commercialization than others. The technologies that are included are:

- SCONOX
- Raper-NOx
- LoTOx
- Activated Carbon Adsorption

### SCONOX

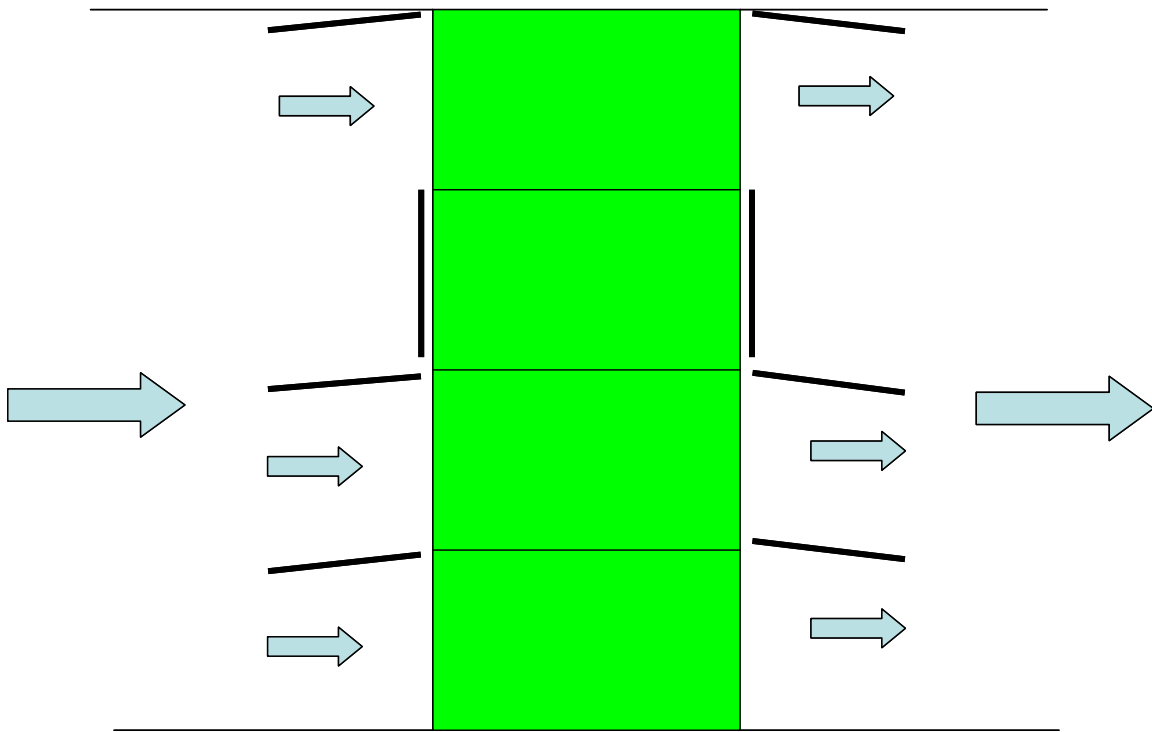
In this document, the technology is referred to by the name most commonly used. In fact, both the name of the company and the technology were changed recently. The name of the company was Goal Line Environmental Technologies, and is now EmeraChem. The technology which was SCONOX is now EM<sub>x</sub><sup>GT</sup> where the GT stands for the application of the product, in this case, gas turbines.

In application, SCONOX has many similarities to SCR with four significant exceptions:

- It does not require a reducing agent
- It reduces the emissions of CO as well as NOx
- It is usually significantly more expensive, both first and operating cost.
- SCR effectivity will diminish as exhaust concentrations get very low, but Sconox will still perform effectively with very low inlet NOx concentrations.

Like SCR, SCONOX is an exhaust gas cleanup technology using a catalytic reactor. Accordingly, it also has little impact on the process, is applicable to almost any combustion source, and is commercially available. However, SCONOX has significant limitations and limited field experience.

SCONOX uses a regenerated catalytic system. The catalytic bed has 2 materials together. A precious metal oxidizing catalyst (usually platinum) and potassium carbonate. The platinum oxidizes the NO into NO<sub>2</sub>. The NO<sub>2</sub> can then be adsorbed onto the potassium carbonate. Once the potassium carbonate is saturated with NO<sub>2</sub>, it must be regenerated with a high hydrogen gas. The hydrogen reacts with the NO<sub>2</sub> to form water and N<sub>2</sub>. The oxidizing catalyst, in addition to oxidizing NO into NO<sub>2</sub>, also oxidizes CO into CO<sub>2</sub>. The system can reduce both NOx and CO by up to 90%.



**Fig. 8-7 SCONOX Chamber Configuration for Regeneration**

The regeneration is part of the operation cycle. The catalyst is contained in separate chambers, usually 4 or groups of 4. Each of these chambers or groups of chambers will be exposed to the exhaust stream for about 15 minutes. At that time, the potassium carbonate becomes saturated with NO<sub>x</sub>. That chamber or group of chambers is then isolated from the exhaust stream by air tight doors, and the high hydrogen regeneration gas is circulated through the chamber (s). The regeneration usually takes about 5 minutes. The first chamber or group is then opened to the exhaust stream, and the second chamber or group of chambers begins regeneration. When the 4<sup>th</sup> chamber or group has completed regeneration, the process is repeated.

The high hydrogen regeneration gas is manufactured at the unit from natural gas using a steam reformer or a natural gas fired reformer.

SCONOX has been demonstrated to reduce NO<sub>x</sub> to less than 2.5 ppmvd (15% O<sub>2</sub>). To achieve these levels, the NO<sub>x</sub> in the engine exhaust cannot be too high, typically less than 25 ppm. It has been successfully applied to:

- Gas Turbines
- Boilers

- Reciprocating Engines

There are several limitations to the application of SCONOX. These include:

- The technology is so intolerant of sulfur that it's impractical on oil fired sources. A typical installation on natural gas will include a sulfur removal section before the NOx catalyst section. The sulfur removal bed is regenerated at the same time and in the same way as the NOx section, with the liberated SO<sub>2</sub> being returned to the exhaust. There is no net change in the SO<sub>2</sub> in the stack.
- The temperature range for this technology is 450 to 700°F.
- As discussed above, the exhaust NOx concentration must be low for the unit to achieve 2.5 ppm.

### **SCONOX Summary**

Advantages:

- Does not use reactant (e.g. ammonia or urea)
- Effectivity does not tail off at low NOx levels
- Demonstrated at less than 2.5 ppm NOx
- Scalable to any size

Disadvantages:

- First cost is higher than SCR
- Operating Cost is higher than SCR
- Catalyst wash every 90 days
- Distillate fuels still a problem
- Can't be used without heat recovery

### **Operating Experience:**

- LM2500 gas turbine – 25 MW over 30,000 Hours
  - Confirmed by EPA and SCAQMD at less than 2.5 ppm on 1 hour rolling average basis
  - Now out of service, not due to SCONOX problems.

- Taurus 60 – 5 MW over 20,000 Hours
  - Liquid fuel operating problems
- 2 – Titans – 13 MW each over 5,000 Hours
  - Operating satisfactorily

## Raper-NOx

In the mid-eighties, the US DOE's Sandia Labs in Livermore CA patented a new back-end NOx control technology. It was purported to not be catalytic. The process consisted of passing the hot exhaust through crystals of cyanic acid, an inexpensive chemical commonly used to treat swimming pools. In the hot exhaust, the cyanic acid crystals break down to form iso-cyanic acid ( $C_2H_5NCO$ ) which reacts with the NOx to form  $CO_2$ ,  $N_2$  and water.

The technology has had several owners over the last 20 years, but has never been offered commercially. In this discussion the process would be classified as SNCR, but at one time, there was a question whether the stainless steel tubing used in the initial development was acting as a catalyst to bring about the reaction. In that case, this technology would have been another form of SCR .

## LoTOx (Ozone Injection)

In looking at this technology, it is interesting to note that NOx is now attainment in almost all areas of the country, so the primary reason for controlling NOx is that it is a precursor to ozone. This technology starts by injecting ozone into the exhaust stream!

The principle is to further oxidize NO and  $NO_2$  into  $NO_3$  which is very soluble in water. The exhaust is then scrubbed to remove the  $NO_3$  and the remaining ozone. Some other benefits are the oxidation of Carbon Monoxide hydrocarbons and organic toxics. The scrubbing process also removed  $SO_2$  and particulate emissions. When it was first introduced, the combustion group of the US EPA was very excited. Here was a technology that removes all of the combustion pollutants at once.

The primary problem associated with the technology is the costs (both initial and operating costs) associated with the scrubbing operation. The only other costs are the ozone generator and controls & monitoring. But, in many applications, the scrubbing process is not cost effective when compared to other NOx control technologies.

The technology has found application in processes that require wet scrubbing for reasons other than NOx control. In those cases, the incremental cost of adding LoTOx is often cost effective in those applications.

This process was developed by several suppliers, but is currently marketed under the LoTOx name by BOC, a supplier of industrial gasses including span gasses.

## **Activated Carbon Absorption with Microwave Regeneration**

Chang Y. Cha of the University of Wyoming has completed several demonstration projects using this technology. It appears to be successful in reducing NOx from a diesel engine, but it has not been progressing toward commercialization.

It consists of alternating beds of activated carbon. The exhaust flows through one while the other is regenerated with microwaves.