

# Applications of Urea-Based SNCR in Hydrocarbon Processing Industry

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The hydrocarbon processing industry is challenged by the task of developing a NO<sub>x</sub> emission control strategy which considers both high and low emission sources, and at the same time reduces the overall cost while meeting current and future NO<sub>x</sub> regulations. Recent advances in selective non-catalytic reduction (SNCR) have made the urea-based SNCR a major technology for NO<sub>x</sub> abatement. The basic chemistry for urea reaction with NO<sub>x</sub> occurs in a high temperature zone which can be found in a furnace between burners and economizer. Comprehensive process design and engineering make highest utilization of the chemical reagent possible. Urea-based SNCR process has been applied successfully on refinery CO boilers, process heaters, package boilers, and waste incinerators. Moderate to high NO<sub>x</sub> reductions with minimum NH<sub>3</sub> slip were achieved under wide temperature and load conditions. Good performance was demonstrated when the combustion sources are characterized by low and high NO<sub>x</sub> baselines generated by regular or waste fuels, and sometimes with large load fluctuations. The urea-based SNCR technology has expanded the options that refinery and petrochemical plants have in developing strategies to meet or exceed current and future NO<sub>x</sub> emission targets.

## INTRODUCTION

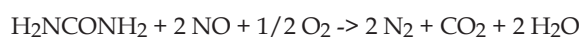
Combustion in the hydrocarbon processing industry produces a wide range of nitrogen oxides (NO<sub>x</sub>) emissions from a large variety of sources. The wide range of NO<sub>x</sub> emissions in a petrochemical plant and refinery could come from sources such as CO boilers, ethylene crackers, process heaters, steam boilers, turbines, as well as waste incinerators. The hydrocarbon processing industry is challenged by the task of developing a NO<sub>x</sub> emission control strategy which considers both high and low emission sources, and at the same time reduces the overall cost while meeting current and future NO<sub>x</sub> regulations. Recent advances in selective non-catalytic reduction

(SNCR) technology have found success in many full-scale combustion systems burning solid, liquid and gaseous fuels. Consequently, many states have recognized urea-based SNCR as a flexible and cost-effective NO<sub>x</sub> reduction process.

## THE UREA-BASED SNCR TECHNOLOGY

**A Major NO<sub>x</sub> Abatement Technology.** Post-combustion NO<sub>x</sub> treatment, particularly the NO<sub>x</sub>OUT<sup>®</sup> process (Figure 1),<sup>1</sup> is a representative urea-based SNCR technology. The technology initially emerged from research on the use of urea to reduce nitrogen oxides by the Electric Power Research Institute (EPRI). Currently, there are thirty five (33) U.S. patents centered around the NO<sub>x</sub>OUT<sup>®</sup> process, and thirty one (31) of them were granted after 1988. The urea-based SNCR has joined other NO<sub>x</sub> abatement methods such as combustion modifications and selective catalytic reduction (SCR), as a major cost-effective NO<sub>x</sub> abatement technology. The NO<sub>x</sub>OUT<sup>®</sup> process has been applied to over one hundred stationary systems with good NO<sub>x</sub> reduction and relatively low cost. Due to continuous mechanical and chemical improvements, the process now can achieve moderate to high NO<sub>x</sub> reductions (50-70% typical, and can be as high as 80-90%) with minimal secondary by-products (≤ 15 ppm NH<sub>3</sub>).

Comparison with Use of Ammonia. Unlike ammonia, urea-based SNCR utilizes an innocuous chemical, relieving safety and handling concerns of gaseous and aqueous ammonia. Like NH<sub>3</sub> used in SNCR and SCR, urea has a discrete temperature window for the process to be effective. The urea-SNCR temperature window is typically between 1,600 and 2,050°F (Figure 2), which can be found in the furnace between burners and economizer. The principal chemical reaction for urea to reduce nitric oxide is expressed as:



As one mole of urea reacts with two moles of NO, a normalized stoichiometric ratio (NSR) of 1 is defined. The temperature window for NH<sub>3</sub> SNCR is almost identical to that of urea, but the NH<sub>3</sub> SNCR window shifts slightly lower (ca. 100°F). The urea-based SNCR process injects a urea solution, which provides an advantage over ammonia. Urea liquid droplets are more heat resistant to higher temperature. The release of urea can be controlled to match the distribution of NO<sub>x</sub> in a furnace. The evaporation rate and penetration of urea droplets are designed with proper particle size and momentum which fit furnace configurations on a case by case basis. This capability improves chemical reagent utilization and eliminates use of mechanical mixing devices such as the ammonia injection grid (AIG) system or large quantities of a driver gas such as air, steam or flue gas recycle. When inappropriately applied, injected urea, as well as ammonia, can be oxidized at excessively high temperatures (e.g. > 2200°F). This will result in an increase in NO<sub>x</sub> formation rather than NO<sub>x</sub> destruction. At low temperatures, by-product of NH<sub>3</sub> can become significant. This is called NH<sub>3</sub> slip (Figure 3).

**Critical Process Parameters.** In addition to temperature, residence time is also a critical process parameter for SNCR. Longer residence time allows a higher completion of urea reaction with NO<sub>x</sub>. Longer residence time also favorably broadens the application temperature window (Figure 4). Applications in refinery furnace heaters and municipal waste combustors are easier applications for SNCR because of their general longer residence time. The urea and NO<sub>x</sub> flame reaction mechanisms are very complex. Major flame reaction pathways can be categorically classified into an ammonia and a cyanuric acid route.<sup>2,4,5</sup> The ammonia route produces amidozine (NH<sub>2</sub>) radicals which then react with NO to form the desirable product nitrogen. The cyanuric acid route leads to intermediates, such as isocyanic and cyanic acid, which may produce a small amount of secondary byproducts such as nitrous oxide (N<sub>2</sub>O) and carbon monoxide (CO).

Carbon monoxide concentration at the point of chemical injection is also important.<sup>2</sup> Carbon monoxide is a measure of the gas phase hydroxyl radical (OH·) concentration, an important intermediate in the NO<sub>x</sub> reduction chemistry. Increasing OH· radical concentration has the effect of shifting the temperature window for either urea or ammonia based systems. In some cases this can be a disadvantage but in many cases this

knowledge can be used for further optimization of the NO<sub>x</sub> reduction process.

**Key Process Features.** The NO<sub>x</sub>OUT<sup>®</sup> program incorporates various scientific methods to accommodate non-ideal situations relative to temperature and residence time. First, influence of common flue gas components on NO<sub>x</sub> reduction as a function of temperature and residence time is experimentally and theoretically determined. These include combustion simulations using pilot combustors and computational fluid dynamic and kinetic modeling. Next, chemical injections at multiple locations with automatic process control allows more efficient response to temperature and load changes. Then, special injector and nozzle designs are used to meet liquid droplet size and chemical distribution requirements for the specific application.<sup>6</sup> The urea-based chemical formulations insure consistent product quality control and include specialty additives which prevent problems such as injector fouling. With these capabilities, urea spray trajectories can closely follow NO<sub>x</sub> distribution profile in the post combustion zone, resulting in a high chemical reaction efficiency. In practice, the accurate predictability minimized field optimization time. With pre-assembled feed equipment in small modules, it offers ease of installation and flexibility in space. Overall, the process performance can typically be demonstrated in two weeks, and installation finished within a time period that does not interfere with normal operation.

The only byproducts that have been observed for SNCR are ammonia, carbon monoxide, and nitrous oxide. All three byproducts are minimized when the temperature is on the high side of the window and residence time is relatively long. Ammonia is of concern because of the possibility of forming ammonium salts (sulfate, bisulfate, and chloride). These salts can foul backend heat exchange equipment or form visible plumes. Carbon monoxide is normally sufficiently low (0-20 ppm) so that it does not create a problem. Nitrous oxide is not included in any regulatory definition of NO<sub>x</sub> but is of concern as a potential greenhouse gas. Formation of N<sub>2</sub>O can range from zero to some 15% of the NO<sub>x</sub> reduced. In most cases, byproducts have been maintained so as to not create any operational or environmental concerns.

**New Advances in Urea-Based SNCR.** More recently, several advanced urea-based technologies were developed to add greater

versatility to the NO<sub>x</sub> compliance strategy employing SNCR. Exemplary advanced processes include the SNCR/SCR Hybrid,<sup>7</sup> the NOxOUT<sup>®</sup> PLUS process,<sup>8</sup> and a urea-slurry process consisting of injecting urea-based chemical with an alkaline slurry.<sup>9</sup> The urea and alkaline slurry process was designed to simultaneously remove NO<sub>x</sub>, SO<sub>x</sub>, and HCl by injecting slurry into the furnace. The NOxOUT<sup>®</sup> PLUS process involves an in-situ thermal treatment of urea, which produces a more kinetically active reagent. The enhanced reagent shows a widened temperature window, in combination with or absence of urea. This treatment also has the advantage of reducing byproducts of nitrous oxide and carbon monoxide. The SNCR/SCR Hybrid process was designed to achieve SCR type of high NO<sub>x</sub> reduction efficiency without the hazards associated with ammonia and with a lower cost than SCR. The pilot test results demonstrated that purposely generated ammonia from the SNCR process can be an effective reducing agent for the downsized catalyst downstream. Since SNCR is used to reduce the majority of the NO<sub>x</sub>, catalyst requirements are reduced. Space velocity and pressure drop designate a smaller catalyst size which can normally be fitted or designed into an economizer and/or air preheater section.

#### UREA-BASED SNCR APPLICATIONS

The urea-based SNCR process can be used to meet the requirements for NO<sub>x</sub> abatement in the hydrocarbon processing industry. The combustion units in refineries and petrochemical plants are usually operated within the effective SNCR temperature window, and with residence time meeting or exceeding the minimum required (Table I). The function of a CO boiler in a refinery is to burnout the refinery offgas containing significant concentrations of CO and volatile hydrocarbons. Process heaters perform heat exchange functions, normally at relatively low heat intensities. Waste incinerators are operated to completely burnout organic waste and hazardous materials. Steam boilers in refineries

and petrochemical plants produce steam for use in various processes and power generation. The steam boiler aspect of urea-based SNCR application is the same as those previously described.<sup>10-12</sup>

**CO Boiler.** This type of boiler burns CO-laden refinery offgas that exits a Fluidized Catalytic Cracking (FCC) unit. Depending upon the steam demand, supplementary firing with refinery off-gas is instituted. Consequently, these units experience a large fluctuation in load swings under normal operating conditions. As burnout within the FCC regenerator has improved in recent years, the CO content of the fuel has declined in many cases. The heat input from CO has been replaced by a variety of refinery fuel gas streams.

Urea-based SNCR performance for a CO boiler has been characterized at high (300 Klbs/hr), medium, and low load, plus "normal" (210 Klbs/hr) conditions. The five observation ports on the CO boiler (Figure 5) were utilized as injection ports. The NO<sub>x</sub> baseline under high load condition was approximately 130 ppm. This was reduced to 60 ppm which represents a 54% NO<sub>x</sub> reduction. NO<sub>x</sub> reductions were in the range of 45-55% throughout the operating conditions using an urea-based reagent (Figure 6). This far exceeds the minimum NO<sub>x</sub> reduction requirement of 24%. Ammonia slip was less than 20 ppm, as measured at the ESP inlet, and was 2-6 ppm at lower loads. The urea-based SNCR performance demonstrated its capability of following frequent load and temperature changes in an adverse low NO<sub>x</sub> baseline situation.

An oxygenated hydrocarbon enhancer was also tested by co-injecting it with the urea-based chemical. The co-injection resulted in 15% additional NO<sub>x</sub> reduction at lower temperatures (1500-1700°F). Particulate measurement at the ESP showed that the urea-based SNCR had no effect on total particulate load or its collection efficiency.

**Process Heaters.** The subject process heaters are

**Table I. Parameters Influencing Urea-Based SNCR Applications in Refineries.**

	<u>CO Boiler</u>	<u>Process Heaters</u>	<u>Waste Incinerators</u>
Temperature, °F	1800-2000	1600-1900	1700-2000
Residence Time, sec	0.3-0.6	0.4-0.8	0.3-1.5
Flue Gas Velocity, ft/sec	15-25	2-8	20-30

located in a refinery which is in an ozone non-attainment area. The No. 1 process heater burns refinery off-gas at 50 MMBtu/hr heat input. The No. 2 heater fires at 177 MMBtu/hr with refinery off-gas and supplemental natural gas. The use of urea-based SNCR reduced NO<sub>x</sub> emissions of No. 1 furnace heater from approximately 100 ppm to 30 ppm or 70% (Figure 6). The NO<sub>x</sub> emissions of No. 2 furnace heater was reduced from 90 ppm to 38 ppm or 58% (Figure 7). This demonstrated the capability of urea-based SNCR in reducing NO<sub>x</sub> from a low baseline of NO<sub>x</sub> in furnace heaters.

The actual tons per year of NO<sub>x</sub> reduced from the No. 2 heater were more than the No. 1 heater because of the larger size of No. 2. This plays a factor in the NO<sub>x</sub> control strategy dealing with individual and total emissions. For this application, the NO<sub>x</sub> reductions were obtained in order to provide offsets for expansion of refinery capacity.

**Waste Incinerator.** Many refinery processes produce a waste sludge containing high levels of acetonitrile (ACN), acrylonitrile (AN), and other waste materials. In the U.S., the ACN and AN in the water constitute a hazardous waste that requires incineration to destruct 99.99% of the ACN and AN.

The urea-based SNCR process was applied on two

similar systems consisting of an absorber offgas (AOG) incinerator and a HRSG (Heat Recovery Steam Generator) burning AOG and an aqueous waste stream containing ACN and AN. A diagram of the AOG incinerator and the injector locations of the urea-based chemical is shown in Figure 8. As noted in the Figure, the AOG ports surround the burner, and so does the Overfire Air (OFA). Through an injector, aqueous ACN/AN stream is atomized to the tip of the burner, where primary combustion air and fuel gas are also added. The AOG fume characteristics are listed in Table II. Combustion of fuel gas incinerates the ACN/AN stream as well as the AOG. At the end, the cylinder narrows as gas exits to the HRSG. To insure complete incineration, the water walls of the waste heat boiler are covered with refractory. The incinerator firing rate is controlled by maintaining the temperatures at the exit of the incinerator to a specified level. The baseline NO<sub>x</sub> varied between 30 to 180 lb/hr or 10 to 350 ppm, depending on the firing rate and ACN/AN flow. The plant intended to control the NO<sub>x</sub> level to a limit of 109 lb/hr. Baseline NO<sub>x</sub> increased as temperature increased. They were 132, 213, and 261 ppm at 1355, 1600,

**Table II. Absorber Off Gas Fume Characteristics**

<u>Component</u>	<u>Normal Volume %</u>	<u>Range Volume %</u>
N <sub>2</sub>	94.17	92.0 - 95.0
CO <sub>2</sub>	2.06	1.5 - 2.5
H <sub>2</sub> O	1.76	1.5 - 2.0
CO	1.24	1.0 - 1.5
Propane (C <sub>3</sub> H <sub>8</sub> )	0.62	0.5 - 1.2
Propylene (C <sub>3</sub> H <sub>6</sub> )	0.14	0 - 2.0
O <sub>2</sub>	0.02	0 - 2.0
HCN ppm <sub>v</sub>	65	40 - 200
Acrylonitrile ppm <sub>v</sub>	10	5 - 150
Acetonitrile ppm <sub>v</sub>	5	2 - 100



1800°F, respectively. The NO<sub>x</sub> reduction results were better at the higher temperatures. When the ACN/AN waste stream was incinerated, the urea-based SNCR provided up to 80% NO<sub>x</sub> reduction at the NSR of 1.9 and 1800°F (Table III). When the feed of waste stream was off, NO<sub>x</sub> reduction was as high as 83% at 1350°F and the NSR of 2, and 97% at 1600°F and at the NSR of 1.9 (Table IV). Ammonia slip was less than 5 ppm. The process reduced NO<sub>x</sub> consistently to levels below the emission limit of 109 lb/hr on both units. In fact, the NO<sub>x</sub> levels were from 150 to 20 lb/hr on Unit #1, and from 160 to 50 lb/hr on Unit #2. This case demonstrated the high performance of urea-based SNCR in a refinery incinerator.

**Table III. NO<sub>x</sub>OUT Performance in Absorber Off Gas Incinerator with Acetonitrile and Acrylonitrile Feed**

Temperature = 1800°F (982°C)		
<u>NSR</u>	<u>ppm NO<sub>x</sub></u>	<u>% NO<sub>x</sub> Reduction</u>
0	261	0
0.5	180	31
1	140	46
1.5	86	67
1.9	53	80

#### COMPLIANCE STRATEGY

In the hydrocarbon processing industry, the urea-based SNCR technology has shown to be capable of controlling NO<sub>x</sub> emissions from high and low NO<sub>x</sub> baselines, under large load fluctuations, as well as with a variety of fuels. Furthermore, the urea-based SNCR can work together with other major NO<sub>x</sub> control methods such as combustion modifications and SCR. These capabilities offer a compliance strategy which may take advantage of current and future NO<sub>x</sub> regulations. The current NO<sub>x</sub> emissions from existing sources may be concentrated on CO boilers, ethylene crackers, and some heavy oil heaters. Reducing NO<sub>x</sub> emissions from these units at high levels may be sufficient enough for the entire plant under the bubble approach. The capability of over-control also may

**Table IV. NO<sub>x</sub>OUT Performance in Absorber Off Gas Incinerator without Acetonitrile/Acrylonitrile Feed**

I. Temperature = 1350°F (732°C)		
<u>NSR</u>	<u>ppm NO<sub>x</sub></u>	<u>% NO<sub>x</sub> Reduction</u>
0	334	0
0.5	236	29
1	180	46
1.4	109	66

II. Temperature = 1600°F (871°C)		
<u>NSR</u>	<u>ppm NO<sub>x</sub></u>	<u>% NO<sub>x</sub> Reduction</u>
0	327	0
0.5	215	34
1	125	62
1.5	36	89

be used as an offset to allow new units to be permitted. In southern California, and perhaps soon in Texas and in other environmentally enlightened states, extra NO<sub>x</sub> tons reduced can be used for future emission reduction credits.

#### CONCLUSION

The urea-based NO<sub>x</sub>OUT<sup>®</sup> process has demonstrated high NO<sub>x</sub> reduction while minimizing NH<sub>3</sub> slip in CO boilers, process heaters, and waste incinerators located in refineries and petrochemical plants. The high performance was achieved under wide temperature and load conditions, as well as low and high NO<sub>x</sub> baselines generated by regular and waste fuels. The simplicity, flexibility, and versatility of the process allowed formation of a compliance strategy that reduces cost while taking advantage of current and future NO<sub>x</sub> regulations.

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## FIGURE CAPTIONS

- Figure 1. Schematic Diagram of NOxOUT System.
- Figure 2. Influence of Temperature on NO<sub>x</sub> Reduction in Urea-Based SNCR Process.
- Figure 3. Ammonia Slip as a Function of Temperature.
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- Figure 9. Diagram of Urea-Based SNCR Application in Absorber Off Gas (AOG)-Heat Recovery Steam Generator (HRSG) Incinerator.

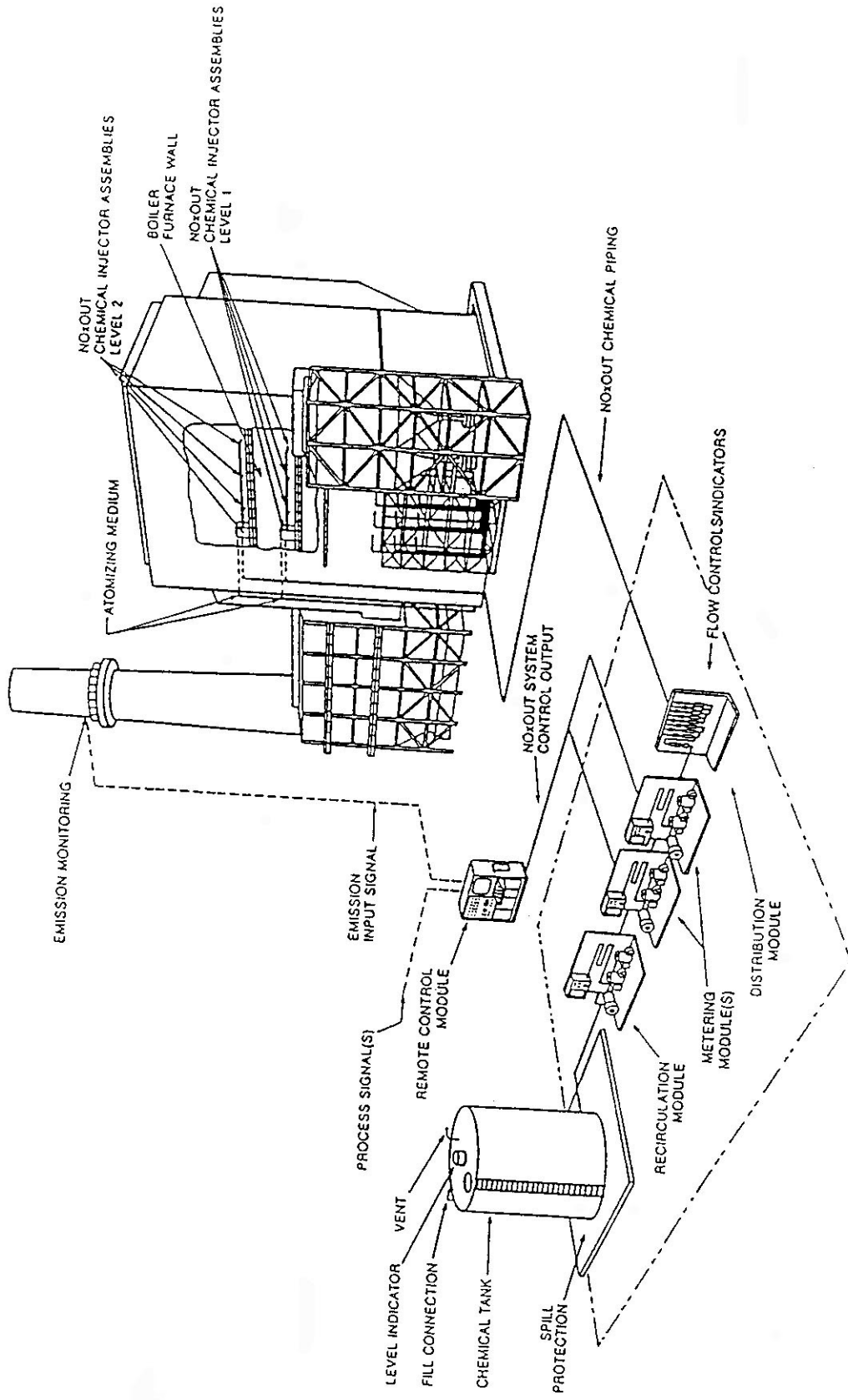


Figure 1. Schematic Diagram of NOxOUT<sup>®</sup> System

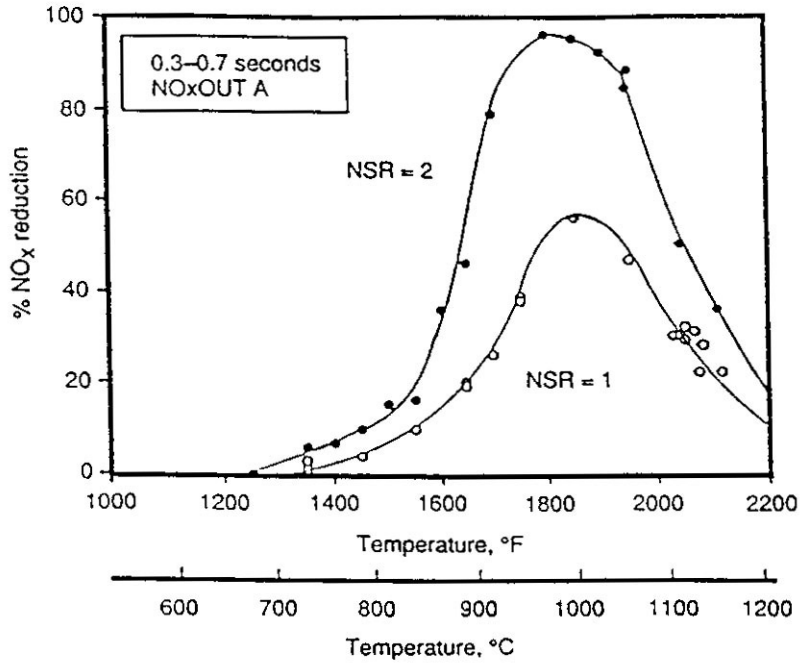


Figure 2. Influence of Temperature on NO<sub>x</sub> Reduction in Urea-Based SNCR Process

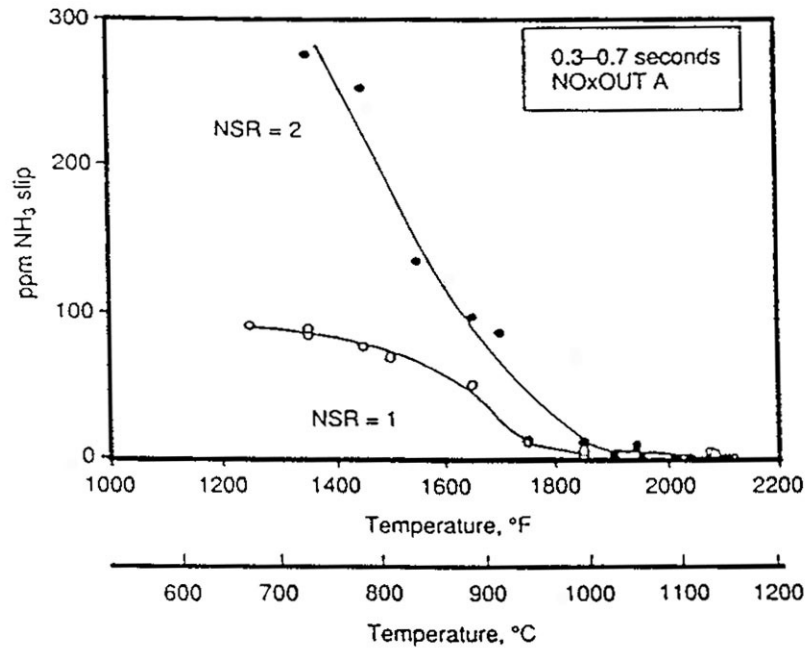


Figure 3. Ammonia Slip as a Function of Temperature



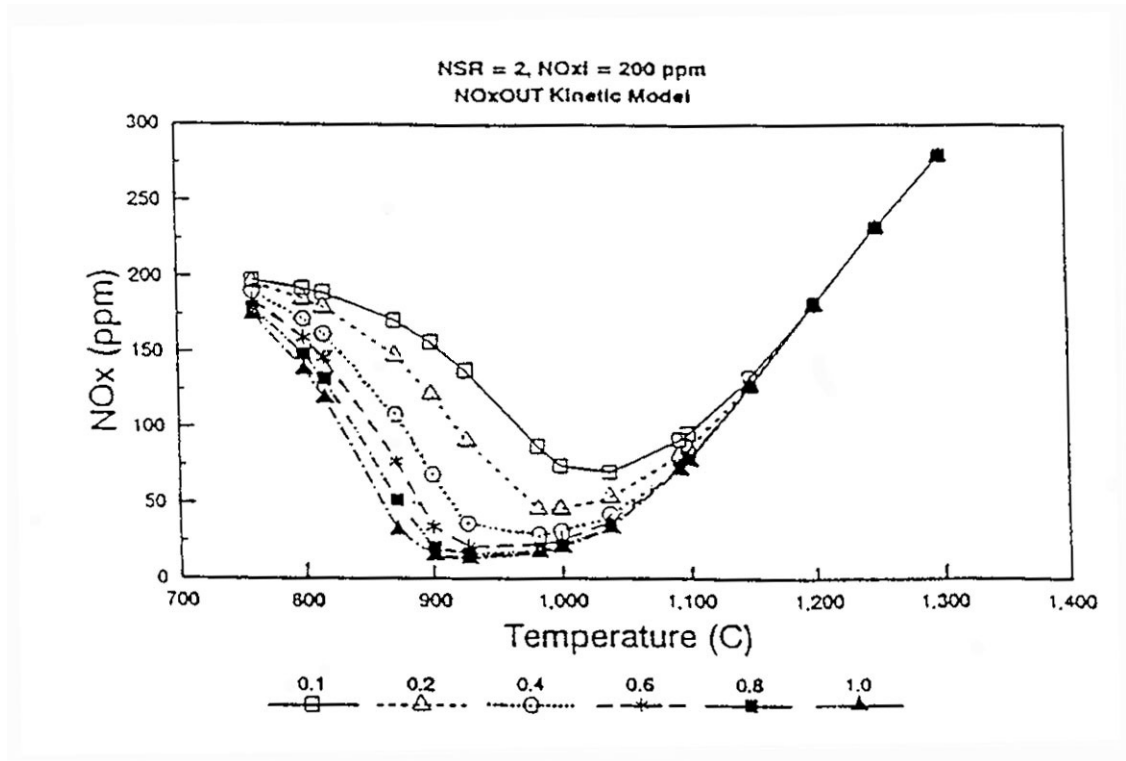


Figure 4. Influence of Residence Time on NO<sub>x</sub> Reduction in Urea-Based SNCR Process

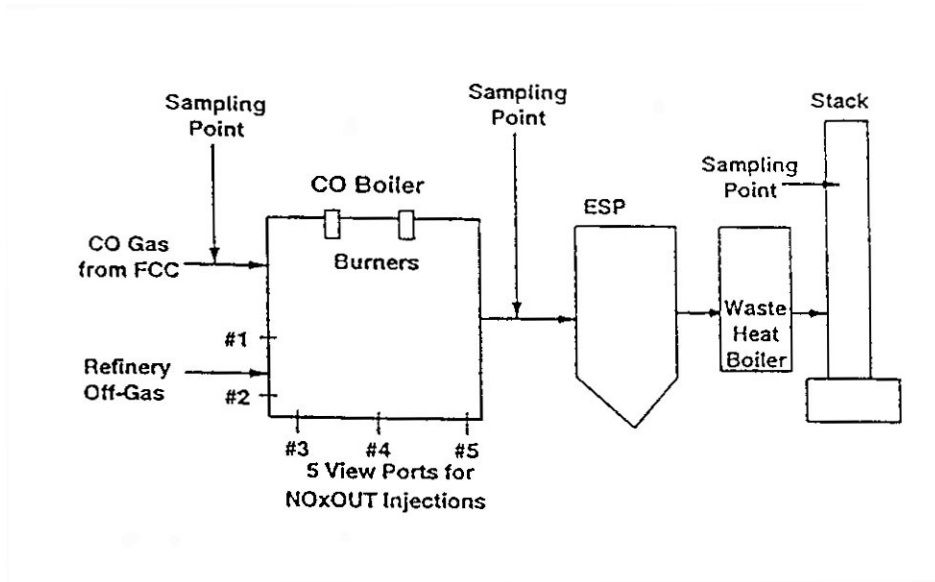


Figure 5. Urea-Based SNCR Application in CO Boiler

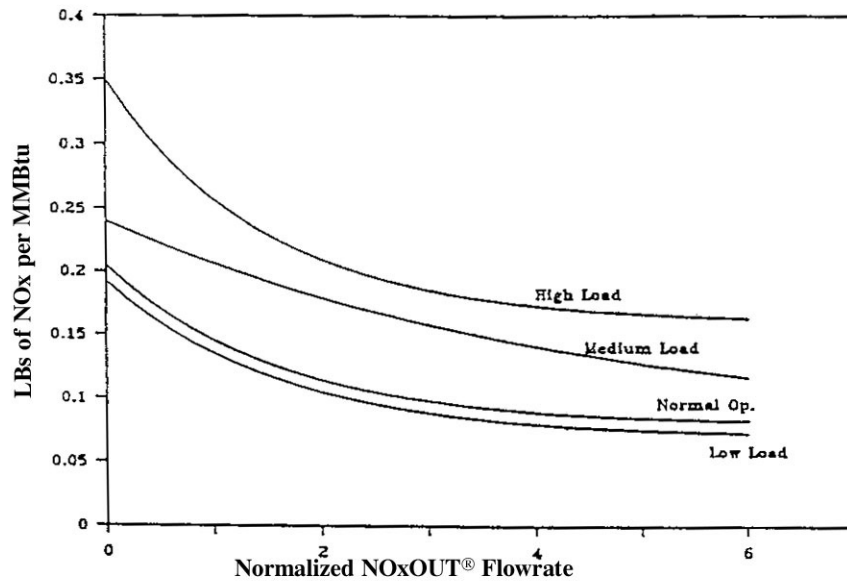


Figure 6. NOx Reduction at Various Loads in CO Boiler

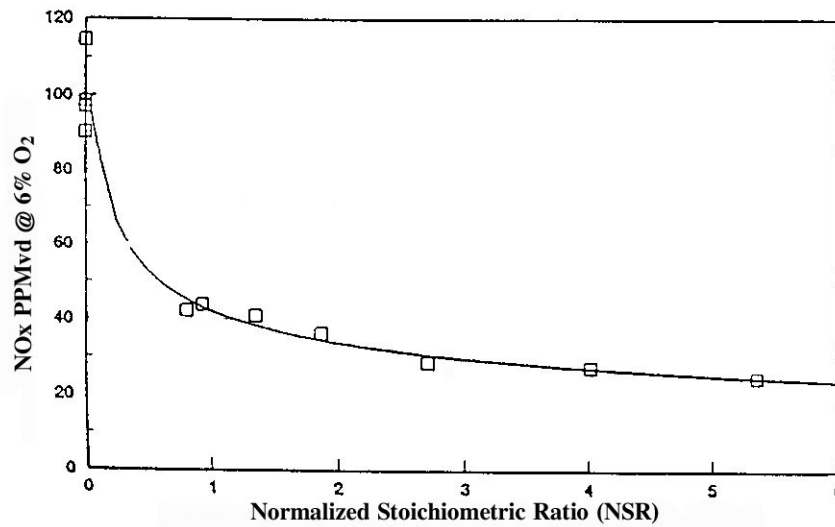


Figure 7. NOx Reduction as a Function of Reagent Dosage in Refinery Furnace Heater No. 1

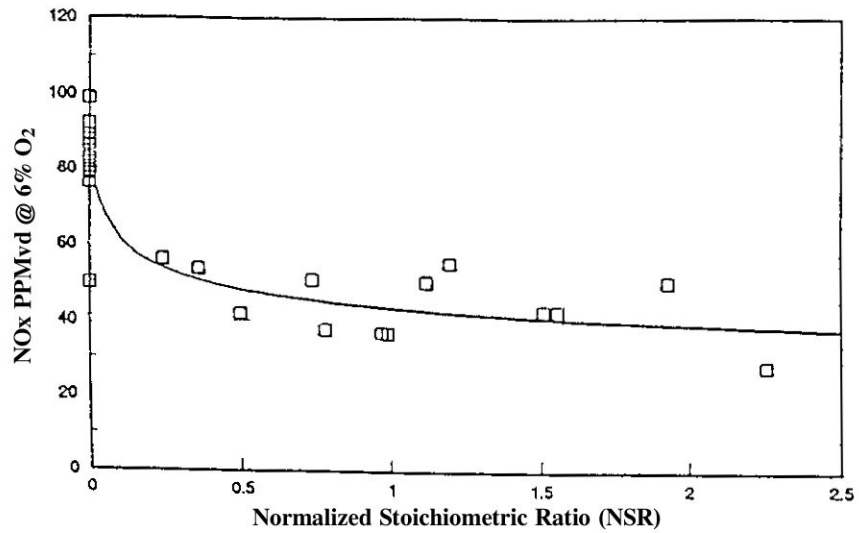


Figure 8. NOx Reduction as a Function of Reagent Dosage in Refinery Furnace Heater No.2

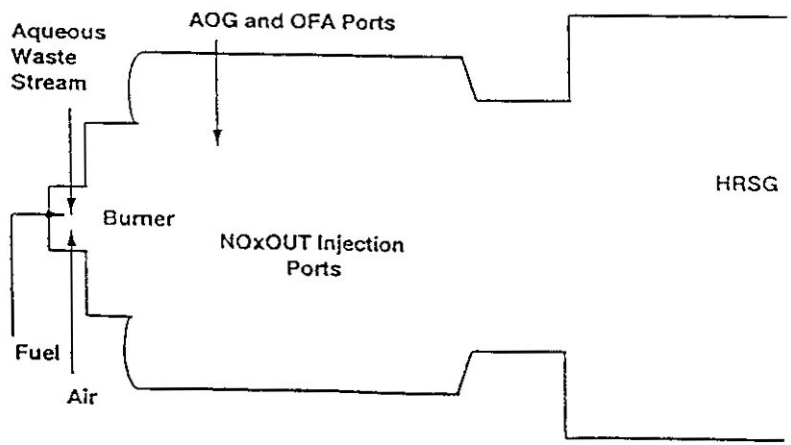


Figure 9. Diagram of Urea-Based SNCR Application in Absorber Off Gas (AOG)-Heat Recovery Steam Generator (HRSG) Incinerator