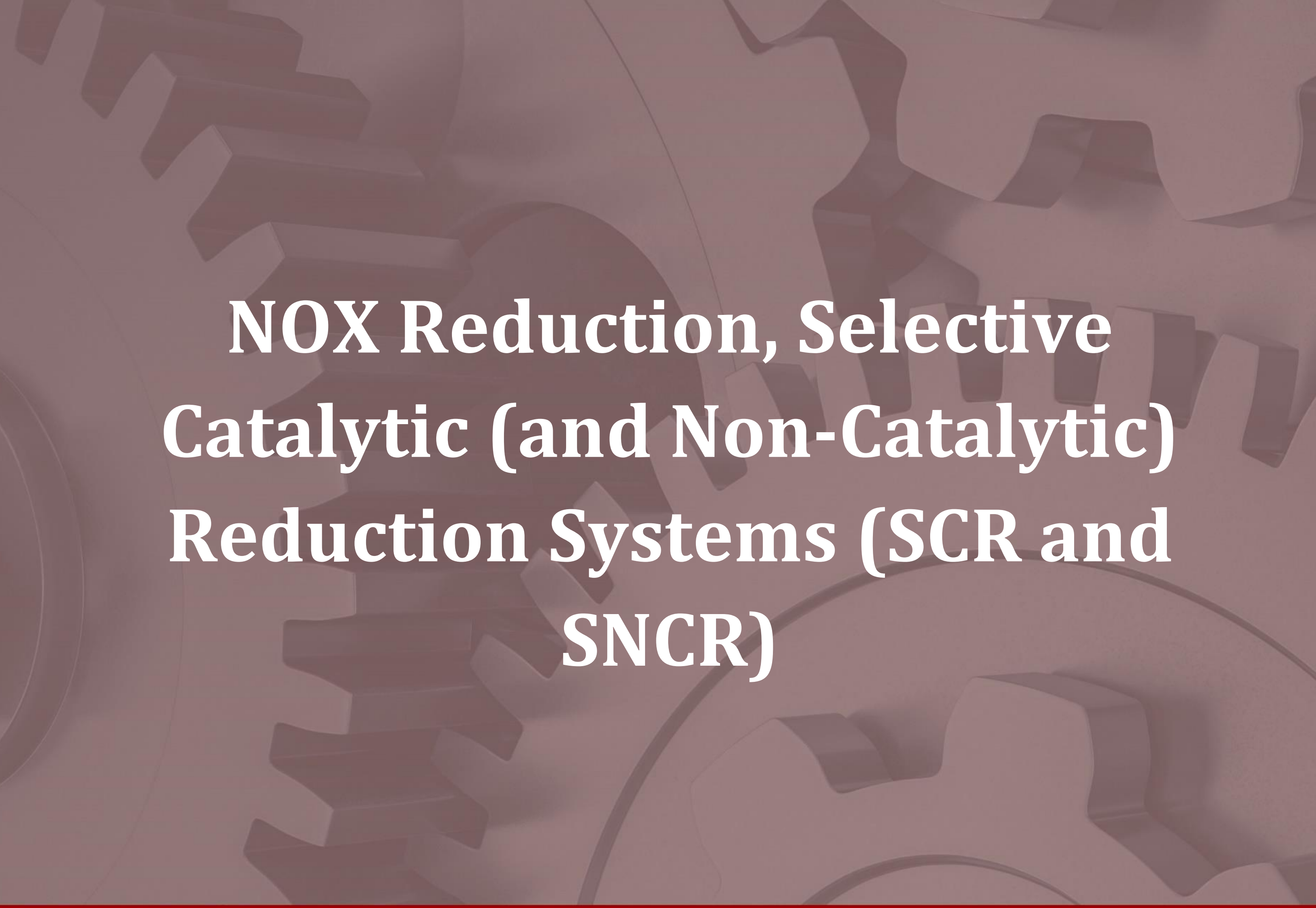
NOX Reduction, Selective Catalytic (and Non-Catalytic) Reduction Systems (SCR and SNCR)

An Online Continuing Education Course for Engineers

Course Number: EN-3040

Credit: 3 Hours / 3 PDH / 3 CPD



NOX Reduction, Selective Catalytic (and Non-Catalytic) Reduction Systems (SCR and SNCR)

Sadegh Sadeghipour, P.E., PhD

NO_X, a product of fossil fuel combustion, has great negative impacts on health, environment, and agriculture. Therefore, NO_X emission control has become an important factor in the design of fossil fuel burning equipment.

Two techniques are normally adopted for controlling/minimizing NO_X emissions from the combustion sources. First is to minimize the NO_X formation by influencing the combustion process in the combustion regions. The second approach, however, relies on chemically converting NO_X emission, after its formation during the combustion process. The first approach is based on the design modifications to reduce NO_X formation during the combustion process. The second approach is based on adding additional systems/equipment to convert NO_X into environmental friendly species.

This training is built around post-combustion technologies for NO_X reduction, namely SCR (Selective Catalytic Reduction) and SNCR (Selective Non-Catalytic Reduction) systems even though reducing NO_X generation by influencing the combustion process is briefly discussed. SNCR and SCR are, in fact, the two main processes commonly used in power plants for high NO_X removals.

SCR and SNCR systems will be discussed in greater details and compared. However, the main focus of this training will still be Selective Catalytic Reduction (SCR) Systems, as this is the most commonly used technique for post-combustion NO_X reduction. Some of the topics which will be covered for the SCR systems will include, process, chemistry, design, operation, maintenance, catalyst management, and cost.

Background Information

Ozone forms in the atmosphere when three atoms of oxygen combine forming O_3. While the chemical structure of ozone is the same; however, two categories of ozone are defined, based on the location where exists (distance from the earth). Stratospheric (good) Ozone is found naturally in the earth's upper atmosphere, 6 to 30 miles above the earth's surface. This Ozone forms a protective layer that shields the earth and its inhabitants from the sun's harmful UV rays.

Tropospheric (bad) Ozone, on the other hand, is formed and found near the ground level (0 to 6 miles). Ground Level Ozone (Smog) is a harmful air pollutant which can cause an acute respiratory problem, aggravate asthma, and impair the immune system. It can damage crops, reducing growth rates and crop yields. Ground-level Ozone is responsible for millions of dollars in reduced crop production in the United States each year.

Bad Ozone forms near the ground level when pollutants (Oxides of Nitrogen, NO_X) chemically react with Volatile Organic Compounds (VOCs) in the presence of sunlight. Emissions from stationary combustion sources such as (electric utility and industrial) boilers and transportation vehicle exhaust are the two major sources of NO_X and VOCs generation. Other contributors of the VOCs release include gasoline vapors, chemical solvents, and biogenic sources (resulting from the activity of living organisms or biological processes, as fermentation).

$$NO_X + VOCs + Sun\ Light = O_3 \qquad \text{(Eqn. 1)}$$

NO_X Formation and Control

NO_X (NO and NO_2, nitrogen monoxide and nitrogen dioxide), a group of highly reactive gases, are the by-product of the combustion of all fossil fuels. During the combustion process nitrogen oxides (NO and NO_2) form in and around the high-temperature regions (around 2600^{o}F), in and around the flame zones. The reaction can briefly be described as:

$$N_2 + O_2 \rightarrow 2NO \qquad \text{(Eqn. 2)}$$

$$2NO + O_2 \rightarrow 2NO_2 \qquad \text{(Eqn. 3)}$$

NO_X normally consists of 95% NO and 5% NO_2. More of these gases form when fuels are burned at higher temperatures. NO_X plays an important role in the atmospheric reactions that create harmful particulate matters, acid rain in the mountain regions, the buildup of nutrients in coastal estuaries leading to oxygen depletion that degrades water quality and harms fishes, and ground-level ozone (smog). NO_X additionally contributes to global warming.

Historically, the quantity of these inorganic compounds in the combustion products was not high enough to affect boiler performance, and as a result, their presence was largely ignored. NO_X emissions, however, are currently regulated by the US states and federal authorities, as well as by most developed countries. NO_X emissions have become an important factor in the design and operation of fossil fuel burning equipment.

Two techniques are normally adopted for controlling/minimizing NO_X emissions from the combustion sources. First is to minimize the NO_X formation by influencing the combustion process in the combustion regions. The second approach relies on chemically converting NO_X emission, after its formation during the combustion process. The first approach is based on design modifications to reduce NO_X formation during the combustion process. The second approach is based on adding additional systems/equipment to convert NO_X into environmental friendly species.

The N_2 contributing to the NO_X formation in a combustion process can originate from either the combustion air or the fuel. Product is called Thermal NO_X, if N_2 is originated from the air, otherwise is referred to as Fuel NO_X. Fuel and thermal NO_X constitute 60-80% and 40-20% of the total NO_X, respectively. The most important design criteria for controlling thermal and fuel NO_X from the coal-burning equipment can be summarized as:

- Coals with lowest Nitrogen content and lowest Oxygen/Nitrogen ratios will generally generate the least amount of NO_X.
- Fuel NO_X generation can be minimized by minimizing the Excess Oxygen. This is done by reducing the amount of air admitted to mixing with coal, in the early stages of combustion.
- The contribution of thermal to total NO_X can be reduced by operating at minimum possible excess air. Additionally, minimizing gas temperature throughout the furnace by using the low turbulence diffusion flames and large water-cooled furnaces will reduce thermal NO_X.

Of the above three factors which might be used to reduce NO_X by influencing the combustion process, the first one might be limited due to the fuel type being burned. Lowering O_2 level and/or reducing combustion temperature are typically used to lower the NO_X generation.

Common technologies used to provide lower NO_X generating combustion environments (lower excess oxygen and dominant temperatures), include: flue gas recirculation, staged combustion, burners out of service, over-fire air, staged air or fuel introduction, and low NO_X burners. Suppressing the N_2 content by O_2 enrichment or by chemical reactor (non-thermal) combustion are emerging technologies for reducing NO_X generation during combustion.

Control of NO_X Emission

Reducing NO_X generation by influencing the combustion process was briefly discussed above. Interested individuals may refer to many available resources for more details. The main purpose of this training, however, is to discuss the post-combustion NO_X reduction (the second approach). In this approach, the NO_X contents of the flue gas are chemically converted, with the help of a reagent. This is achieved by introducing a reducing agent into the combustion product to react with NO_X emissions to produce atmospheric N_2 and water vapor. Ammonia species (Anhydrous NH_3, Aqueous NH_3, or Urea) are preferred over other chemicals, as a reducing agent, due to their selective nature (Ammonia's preference for reacting with NO_X, overreacting with Oxygen), relatively low cost, and water byproduct.

If ammonia reacts with NO_X in the presence of a catalyst, this technology is called SCR (Selective Catalytic Reduction). If no catalyst is involved, the technology is then called SNCR (Selective non-Catalytic Reduction). For SNCR (also called Thermal DeNOX), the reaction needs to take place at a higher temperature, as compared to SCR. SCR has a higher capital cost, particularly due to the catalyst costs; however, SNCR has a higher operating cost due to higher reagent consumption.

Both SCR and SNCR have higher capital and operating costs as compared to other techniques used to reduce NO_X generation from combustion. However, at the same time, SNCR and SCR, with 30-50% and about 80-90% NO_X removal capabilities, respectively, are very efficient technologies for removing NO_X. The decision between using SCR or SNCR is made based on the boiler and fuel types as well as the desired level of NO_X reduction.

Benefits of the SNCR system include lower capital equipment cost, simple operation, and minimal impact on the boiler operation. The SNCR operating cost is mainly related to its reagent consumption. In addition to lower NO_X removal capability, the other downsides of the SNCR system include limited retrofit ability and problems related to changes in load and other operating conditions.

In addition to higher NO_X removal capability, other benefits of the SCR system include easier retrofit ability and being tolerant of loading changes, and relatively simple to operate. High capital equipment cost, sensitivity to fuel quality, and greater impact on the boiler operation are the downsides of the SCR systems. Reagent consumption, catalyst replacement, and operating draft losses constitute the SCR operating costs.

Selective Non-Catalytic Reduction (SNCR) Systems

SNCR process takes place in the boiler, immediately downstream of the combustion zone, where the flue gas temperature is high enough for the process to occur. Ammonia or urea is injected into the flue gas through multiple points, to react with NO_X (Figure 1). SNCR systems have been used for large (coal, gas, and oil) utility and industrial boilers, as well as for waste and sludge incinerators. A simplified presentation of the reactions taking place between the reagent and NO_X can be given by the following equations.

Ammonia:

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O \qquad \text{(Eqn. 4)}$$

Urea:

$$4NO + 2NH_2CONH_2 + O_2 \rightarrow 4N_2 + 4H_2O + 2CO_2 \qquad \text{(Eqn. 5)}$$

SNCR systems may use either ammonia (anhydrous or aqueous) or urea as their reducing agent. Therefore based on the reagent used, two SNCR systems may be differentiated. In anhydrous ammonia systems, vaporized ammonia is blended with air or steam before injection into the boiler flue gas. But, in aqueous ammonia systems, ammonia solution (concentration not more than 29%) is directly injected into the flue gas, evaporating after injection.

In urea systems, dry urea supplies are first converted into solutions of typically 50% concentrations. The solutions then evaporate as injected into the boiler flue gas.

The SNCR reactor is expected to accomplish the following four tasks.

1 – Mixing the reagent throughout the flue gas stream,

2 – Evaporating the reagent (if is liquid),

3 – Decomposing the reagent into ammonia free radicals,

4 – Reacting the free radicals with NOX

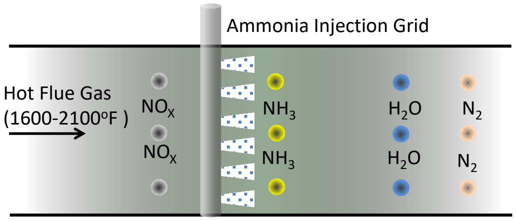


Figure 1: NOX reacts with injected reactant, in SNCR reactor, producing water and nitrogen.

Using ammonia as a reagent, the SNCR process chemistry may be summarized as,

Decomposition:

$$NH_3 + OH \leftrightarrow NH_2 + H_2O \qquad \text{(Eqn. 6)}$$

$$NH_3 + O \leftrightarrow NH_2 + OH \qquad \text{(Eqn. 7)}$$

$$H + NH_3 \leftrightarrow NH_2 + H_2 \qquad \text{(Eqn. 8)}$$

NOX reduction reactions:

$$NH_2 + NO \rightarrow N_2 + H_2O \qquad \text{(Eqn. 9)}$$

$$NH_2 + NO \leftrightarrow HN_2 + OH \qquad \text{(Eqn. 10)}$$

$$HN_2 \rightarrow N_2 + H \qquad \text{(Eqn. 11)}$$

Optimum design of the reagent injectors is one of the most critical aspects of the SNCR systems. Of primary consideration are the placement of the injectors and their relation to the boiler arrangement. This should provide proper temperature and sufficient residence time to drive the chemical reaction. Other important design factors include the injector nozzle design/selection, spray pattern, as well as the droplets size and velocity. The reducing agent should be distributed across the reaction zone blending with the flue gas.

Process Effects in SNCR

It is worthwhile mentioning that in certain cases, NO_X reduction level for SNCR has even approached 75% however, for the majority of the applications, the SNCR efficiency is typically within 30-50%. Reason for the lower actual SNCR efficiency is the difference in the operating condition for different applications. Operating parameters such as exhaust gas temperature, velocity profile and composition, SNCR reactor residence time, the amount of NO_X to be removed, the reagent injected, and many more, all impact the SNCR efficiency. A few of the more important parameters are discussed below.

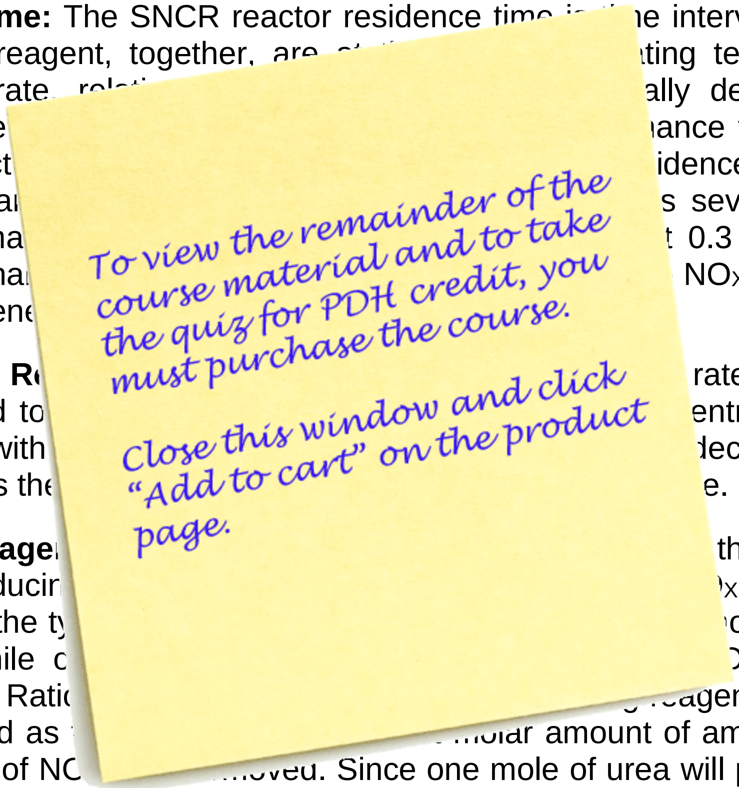
Temperature: Chemical reaction in the SNCR is highly dependent on temperature. The best temperature range is normally 1600ºF to 2100ºF however it may change based on the reagent being used. Operating temperature range and rate of NO_X removal may also be modified by using additives. The SNCR operating temperature being too high may cause ammonia to oxidize forming, instead of removing, NO_X, equation 12. On the other hand, very slow reaction kinetics at low operating temperatures will result in low NO_X removal and a high level of ammonia slip. High ammonia slip will increase the risk of fly ash contamination. A direct consequence of this can be a loss of market value due to odor/health.

$$NH_2 + O \leftrightarrow NO + 2H \qquad \text{(Eqn. 12)}$$

Residence Time: The SNCR reactor residence time i he interval when the exhaust gas and the reagent, together, are ting temperature. Flue gas volume flow rate, relati ally determines the SNCR residence time ance for occurrence of the NH_2-NO_X react idence time for the SNCR applications ca s several seconds. SNCR applications ma t 0.3 seconds. Residence times longer tha NO_X reduction; therefore, it will not be bene

Inlet NO_X and Re rate for NO_X reduction is directly related to entration. NO_X reduction will increase with decreases NO_X removal rate, as well as the e.

Reducing Reage the ratio of the molar amount of reducin x to be removed. SR changes with the ty onia can remove one-mole NO_X while c Ox. NSR (Normalized Stoichiometric Ratio eagents can be compared. NSR is defined as molar amount of ammonia relative to the molar amount of NO moved. Since one mole of urea will produce two moles of equivalent ammonia, NSR is 1 for ammonia and 2 for urea.



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