NOx Emissions control for coal-fired boilers

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Abstract— Nitrogen oxides (NOx) are a very interesting and prevalent family of air polluting chemical compounds. This report explains why NOx are important air pollutants and how NOx are formed and react in the atmosphere. This report also discusses the principles on which all NOx control and pollution prevention technologies are based. This report reviews NOx control technologies for these boilers. It discusses the established commercial primary and secondary control technologies and examines what is being done to use them more effectively. The popular primary control technologies which are in use in the United States are low-NOx burners and overfire air. The secondary NOx control technologies applied on coal-fired utility boilers include reburning, selective noncatalytic reduction (SNCR), and selective catalytic reduction (SCR).

Keywords— SCR, SNCR, LNB, OFA, Reburning

I. INTRODUCTION

A pulverized coal-fired boiler is an industrial or utility boiler that generates thermal energy by burning pulverized coal (also known as powdered coal or since it is as fine as face powder in cosmetic makeup) that is blown into the firebox. Coal is one of the most vital and abundant energy sources in the world. Raw coal contains carbon (C), nitrogen (N), sulfur (S), ash, small amounts of mercury (Hg) and some other elements. Once these elements undergo a combustion process with air, pollutants such as NOx, SO₂ and SO₃ and are formed.[3]

1.1 Why should we control NOx?

NO₂ is the most prevalent form of NOx in the atmosphere that is generated by anthropogenic (human) activities. It reacts in the atmosphere to form ozone (O₃) and acid rain. It is necessary to note that the ozone that we want to minimize is tropospheric ozone; that is, ozone in the ambient air that we breathe. We are not talking about stratospheric ozone in the upper atmosphere that we cannot breathe. Stratospheric ozone protects us and the troposphere from ionizing radiation coming from the sun.[1]

1.2 Where does NOx come from?

About half of the NOx that is emitted is from Automobile and mobile sources. Electric power plant boilers produce about 40% of the NOx emissions from stationary sources. Additionally, substantial emissions are also added by such anthropogenic sources as industrial boilers, incinerators, gas turbines, reciprocating spark ignition and Diesel engines in stationary sources, iron and steel mills, cement manufacture, glass manufacture, petroleum refineries, and nitric acid manufacture. Biogenic or natural sources of nitrogen oxides include lightning, forest fires, grass fires, trees, bushes, grasses, and yeasts. These various sources produce differing amounts of each oxide. The anthropogenic sources are approximately shown as:

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<th>Table 1: Sources of NOx Emissions</th>
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<td>Mobile Sources</td>
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In all combustion there are three opportunities for NOx formation. They are:

- thermal NOₓ
• fuel NO\textsubscript{x}
• prompt NO\textsubscript{x}

Thermal NO\textsubscript{x} formation, which is highly temperature dependent, is recognized as the most relevant source when combusting natural gas. Fuel NO\textsubscript{x} tends to dominate during the combustion of fuels, such as coal, which have a significant nitrogen content, particularly when burned in combustors designed to minimise thermal NO\textsubscript{x}. The contribution of prompt NO\textsubscript{x} is normally considered negligible. A fourth source, called feed NO\textsubscript{x} is associated with the combustion of nitrogen present in the feed material of cement rotary kilns, at between 300° and 800 °C, where it is also a minor contributor.

II. CASE STUDY

NO\textsubscript{x} Control Technologies:- In general, NO\textsubscript{x} control technologies may be placed in two categories: primary and secondary control technologies. Primary control technologies reduce the amount of NO\textsubscript{x} produced in the primary combustion zone. On the other hand, secondary control technologies reduce the NO\textsubscript{x} present in the flue gas away from the primary combustion zone. Some of the secondary control technologies actually use a second stage of combustion, such as reburning.[2]

2.1 Primary Control Technologies: For NO\textsubscript{x} emissions control, popular primary technologies are low-NO\textsubscript{x} burners (LNB) and OFA. These technologies use staged combustion techniques to reduce NO\textsubscript{x} formation in the primary combustion zone. LNB and OFA are described below. The optimum control system design may incorporate one or both of these, selected based on the capacity of the unit, fuels to be fired, and NO\textsubscript{x} reduction requirements.

2.1.1 LNB: A LNB limits NO\textsubscript{x} formation by controlling the stoichiometric and temperature profiles of the combustion process. This control is achieved by design features that regulate the aerodynamic distribution and mixing of the fuel and air, thereby yielding one or more of the following conditions: (1) reduced oxygen in the primary flame zone, which limits both thermal and fuel NO\textsubscript{x} formation; (2) reduced flame temperature, which limits thermal NO\textsubscript{x} formation; and (3) reduced residence time at peak temperature, which limits thermal NO\textsubscript{x} formation. In general, LNBs attempt to delay the complete mixing of fuel and air as long as possible within the constraints of furnace design. This is why the flames from LNBs are usually longer than those from conventional burners. Conceptually, working of an LNB with gradual mixing of combustion air to a fuel-rich flame core is shown schematically in Figure 1. The hardware used to influence the fuel/air mixing varies from manufacturer to manufacturer. LNBs can provide NO\textsubscript{x} reductions of 50% or more from uncontrolled levels, with higher reductions possible for boilers with more facilitating design features.

2.1.2 OFA: OFA, stands for Opposed Fire Air, also referred to as air staging, is a combustion control technology in which a fraction, 5–20%, of the total combustion air is diverted from the burners and injected through ports located downstream of the top burner level. OFA is used in conjunction with operating the burners at a lower-than-normal air-to-fuel ratio, which reduces NO\textsubscript{x} formation. The OFA is then added to achieve complete combustion. OFA can be used in conjunction with LNBs.
The addition of OFA to LNB on wall-fired boilers may increase the reductions by an additional 10–25%.

LNB with Multilevel OFA: A concentric firing system with multilevel OFA is now available for tangentially fired boilers. This combustion technology has achieved NOx emissions <0.15 lb/106 Btu, equating to >60% reduction, while firing PRB subbituminous coal, which reflects the potential for achieving low-NOx emissions with this technology.

Rotating Opposed Fire Air: The rotating opposed fire air (ROFA) design injects air into the furnace first to break up the fireball and then to create a cyclonic gas flow to improve combustion. The difference between ROFA and conventional OFA is that ROFA uses a booster fan to increase the velocity of air to promote better mixing in the furnace. Specific advantages of ROFA include more even distribution of combustion products, less temperature variation across the furnace, and less excess air needed for complete combustion.[2]

2.2 Secondary Control Technologies: For many coal-fired boilers, it may not be possible to achieve sufficiently low-NOx emissions to comply with existing or future NOx regulations by using primary control technologies and/or combustion improvement techniques alone. These units may require secondary controls (with or without primary controls).

Popular secondary control technologies are reburning, selective noncatalytic reduction (SNCR), and selective catalytic reduction (SCR). These technologies are described below.

2.2.1 Reburning: In reburning up to 25% of the total fuel heat input is provided by injecting a secondary (or reburning) fuel above the main combustion zone to produce a slightly fuel-rich reburn zone with a stoichiometry of 90% theoretical air. Combustion of reburning fuel at fuel-rich conditions results in hydrocarbon fragments, which react with a portion of incoming NOx to form hydrogen cyanide (HCN), isocyanic acid (HNCO), isocyanate (NCO), and other nitrogen-containing species. These species are ultimately reduced to \( N_2 \). Finally, completion air is added above the burn zone to complete burnout of reburning fuel. The burning process is shown schematically in Figure 2. Furnace dimensions impact several key design parameters for reburning systems, including mixing of reburn fuel and flue gas, gas residence time within the burn and burnout zones, and heat transfer in the burner zone and the upper furnace. Sufficient residence time is required to achieve adequate flue gas mixing, to accommodate the NOx reduction kinetics in the reburning zone, and for complete combustion in the burnout zone. Given sufficient time in the reburn zone, reburn zone stoichiometry is another critical parameter that influences NOx reduction. This stoichiometry is directly related to the heat input split between the primary and reburn zones.

![Figure 2: Schematic of reburning application.](https://example.com/figure2.png)
carbon burnout (CO or fuel) that may result from the addition of relatively large amounts of reburn fuel needed to achieve the desired NOx reduction; and (3) the potential for increased boiler tube corrosion within the reburn zone.[2]

2.2.2 SNCR: SNCR is a postcombustion technology in which a reagent (ammonia [NH3] or urea) is injected into the furnace above the combustion zone, where it reacts with NOx to reduce it to N2 and water. In general, SNCR reactions are effective in the range of 1800–2100°F. The high temperature necessary for the reaction to proceed requires that the reagent normally be injected into the upper furnace region of the boiler, as shown in Figure 3. Although the actual reactions are more complex, the overall stoichiometric reactions for urea and NH3 SNCR are:

\[
\text{(NH}_2\text{)}_2\text{CO} + 2\text{NO} + 1/2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{CO}_2 + 2\text{N}_2 \\
2\text{NH}_3 + 2\text{NO} + 1/2\text{O}_2 \rightarrow 2\text{N}_2 + 3\text{H}_2\text{O}
\]

In general, NH3 may reduce NOx, oxidize to form NOx, or remain unreacted and pass through the stack. This unreacted portion is referred to as “NH3 slip.” Inadequate flue gas temperature and/or reaction time for SNCR kinetics and mixing of the reagent with flue gas can contribute to an increase in NH3 slip. Relatively high concentrations of NH3 slip can react with SO2 and sulfur trioxide (SO3) in the flue gas and form ammonium sulfates and bisulfates, which, in turn, can cause plugging of the air preheater (APH) passages.

Although the dominant reactions in the SNCR process result in the reduction of NOx to N2, a significant competing reaction is the oxidation of the SNCR reagent to form NOx. This oxidation reaction becomes more significant at relatively higher temperatures. Because of this competing oxidation reaction, there is not a one-to-one relationship between reagent injected and NOx reduced.

**Figure 3: Schematic of a SNCR application.**

Urea reagent is injected as an aqueous solution. NH3 can be injected as a gas (anhydrous NH3) or as an aqueous solution. In general, mixing of flue gas with injected aqueous solution of NH3 or urea is better than that with injected anhydrous NH3. This is because aqueous droplets penetrate farther into flue gas than gaseous anhydrous NH3. Furthermore, because a urea solution is less volatile than a NH3 solution, its droplets generally penetrate farther into the flue gas. Because of somewhat poorer mixing in SNCR systems with NH3 injection compared with those using urea, the former require more elaborate injection schemes in the boiler. Boiler load changes can impact the performance of an SNCR application because of changes in two key parameters: temperature of flue gas at the furnace exit and gas residence time in the furnace. Therefore, the following two measures are usually included in the design of SNCR systems: (1) a multilevel injection system, and (2) an ability to change the amount of reagent to be injected.
SNCR has been applied in the United States on a wide variety of boilers firing a range of fuels. A summary of available SNCR performance data is shown in Figure 4. These data show that NOx reduction efficiencies of these SNCR systems ranged from 15 to 66%. Data also show that whereas smaller boilers (e.g., 78 and 76 MW Salem Harbor units 1 and 2) may be able to achieve >60% NOx reduction, larger boilers (e.g., 500 MW Cardinal Unit 1) may be capable of achieving reductions of only ~30%.[2]

2.2.3 SCR: SCR is a post-combustion NOx reduction technology in which NH₃ is added to the flue gas, which then passes through layers of a catalyst. The NH₃ and NOx react on the surface of the catalyst, forming N₂ and water. SCR reactions are generally effective in a temperature range of 650–750 °F. In general, SCR is capable of providing high levels of NOx reduction, ranging from 80% to >90%. The overall stoichiometric SCR reactions are:

\[ 2\text{NH}_3 + 2\text{NO} + \text{O}_2 \rightarrow 2\text{N}_2 + 3\text{H}_2\text{O} \] (3)

\[ 4\text{NH}_3 + 2\text{NO}_2 + \text{O}_2 \rightarrow 3\text{N}_2 + 6\text{H}_2\text{O} \] (4)

Note that the NOx reduction reactions above are the same as the ones occurring in SNCR at higher temperatures, but the SCR catalyst makes them effective at lower temperatures. In most utility boiler applications, the catalyst is installed in a separate reactor positioned downstream of the boiler economizer and immediately upstream of the APH (see Figure 5). Under low-load conditions, an economizer bypass is sometimes used to ensure proper flue gas temperature at the SCR reactor inlet. The installation shown in Figure 4 is called a “high-dust” SCR installation. A “low-dust” application may be used at facilities with hotside electrostatic precipitators (ESPs). In this case, the SCR reactor would be installed immediately downstream of the ESP and before the APH. An alternative is a “tail-end” SCR installation in which the SCR reactor is located after the flue gas desulfurization system.
Figure 5: Schematic of a SCR application.

An NH3 injection grid is located upstream of the SCR catalyst. As the flue gas with NH3 passes through the catalyst, which may be of the ceramic honeycomb or coated parallel metal plates construction, it provides the active sites (typically vanadia–titania \( \text{V}_2\text{O}_5–\text{TiO}_2 \)) where the NH3 and NOx reduction reactions take place. At the temperature where this reduction occurs, the competing NH3 oxidation reaction is not significant. This results in two advantages over SNCR: much lower outlet NOx concentrations are possible and NH3 slip can be reduced. Because most of the NOx is in the form of NO in coal-fired boilers, the ratio of NH3 added to NOx reduced is typically close to 1:1 (see eq 4). The local molar ratio of NH3 to NOx in the flue gas has a great impact on SCR performance. This process parameter becomes more critical for SCR systems designed for high-reduction efficiencies.

Catalyst deactivation occurs as a result of impurities in the gas stream that can cause poisoning of the catalyst material or blinding deposits. Therefore, catalyst management plans are used at SCR installations to maintain the needed catalyst activity while minimizing costs. In such plans, the catalyst is usually installed in layers to permit the periodic replacement of portions of the total catalyst loading. In certain designs, an empty layer is provided to allow the addition of catalyst to this layer while maintaining the existing catalyst with reduced effectiveness in place over a longer period of time.

SCR has been extensively used to control NOx from hundreds of utility and industrial boilers in Japan and Germany and in several U.S. coal-fired and gas-fired utility boilers. Deployment of SCR at U.S. coal-fired plants for new and retrofit applications initially took place in 1991 and 1993, respectively. Since then, >150 SCR systems have been installed on utility coal-fired boilers. Many of these applications are designed to provide NOx reductions of \( \geq 80\% \), sometimes as much as 90% reduction, with <2 ppm NH3 slip.

The data in this table reflect that in 2003 these units achieved NOx emission rates between 0.04 and 0.07 lb/106 Btu, likely with NOx reduction efficiencies 85%.[2]
III. CONCLUSION

This paper reviewed the technologies for NOx emissions control for coal fired boiler. These technologies involve Primary and Secondary Technologies. We also examined what can be done to use them more effectively. The popular primary control technologies in use in the United States are low-NOx burners and overfire air. Data reflect that average NOx reductions for specific primary controls have ranged from 35% to 63% from 1995 emissions levels. The secondary NOx control technologies applied on U.S. coalfired utility boilers include reburning, selective noncatalytic reduction (SNCR), and selective catalytic reduction (SCR). Thirty-six U.S. coal-fired utility boilers have installed SNCR, and reported NOx reductions achieved at these applications ranged from 15% to 66%. Recently, SCR has been installed at >150 U.S. coal-fired utility boilers. Data on the performance of 20 SCR systems operating in the United States with low-NOx emissions reflect that in 2003, these units achieved NOx emission rates between 0.04 and 0.07 lb/106 Btu.

REFERENCES