OXIDES OF NITROGEN: FORMATION AND CONTROL IN RESOURCE RECOVERY FACILITIES

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ABSTRACT

The control of emissions of oxides of nitrogen from resource recovery facilities is becoming an increasingly important consideration in environmental permitting of new facilities. California presently has strict emission standards in place and other states are considering such standards. This paper reviews the theory of solid fuel combustion, and NOx formation and control in the context of solid waste combustion. The paper further discusses available control technology and its application to facilities burning solid waste.

INTRODUCTION

Air pollution regulations for municipal solid waste incinerators and resource recovery facilities has, in the past, concentrated primarily on controlling particulate emissions. Within the past few years, however, increasing attention has been given to the control of acid gases (SO2, HCl, HF), hydrocarbons (HC) and oxides of nitrogen (NOx). Because NOx emissions are perhaps the most difficult to control of these pollutants, they are of particular interest in resource recovery facilities. The already difficult control problem is exacerbated in resource recovery facilities by the variable composition of the solid waste.

The California Air Resources Board (CARB) has issued guidelines for the many Air Pollution Control Districts in the state which call for NOx emission limits as low as 140 ppm (dry volume, 12 percent CO2, 8 hr average). Manufacturers of solid waste combustion equipment have stated that consistently meeting such a low emission limit without post-combustion control equipment would be difficult if not impossible, even though CARB does not consider the available post-combustion control equipment to be adequately demonstrated on municipal solid waste combustion facilities [1]. The state of California also has regulations in place which require new facilities to demonstrate that a 1 hr ambient air quality standard for NOx of 470 µg/m3 will not be exceeded at any point in the surrounding environment as a result of emissions from the proposed facility. A 1 hr standard such as this is very difficult to meet.

For the rest of the country, there are no NOx emission limits for municipal solid waste combustion facilities. However, new resource recovery facilities must demonstrate that the National Ambient Air Quality Standard for NOx of 100 µg/m³ (annual average) will not be exceeded at any point in the surrounding environment.

The control of emissions of oxides of nitrogen from resource recovery facilities is a subject which deserves attention from the resource recovery industry. Even though there are no national emission limits for NOx from resource recovery facilities as yet, it is clear that many resource recovery facilities which will be built in the future will be subjected to some manner of restriction on NOx emissions whether by regulation or by public pressure. The control of NOx from resource recovery facilities in California is already a difficult problem.

The purposes of this paper are to:

(1) Examine the theory of solid waste combustion and typical mechanisms for accomplishing combustion in resource recovery facilities;
(2) Examine NOx formation theory and current research into control methods; and
(3) Discuss available control technology and its applicability to resource recovery facilities.

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In a mass burn resource recovery facility, raw waste is fed (usually by gravity) down a series of moving grate sections in a variety of proprietary designs developed especially for municipal solid waste. Figure 2 illustrates a typical mass burn design. Underfire air is introduced below the grates and overfire air above the fuel bed.

FIG. 1 TYPICAL TRAVELLING GRATE, SEMI-SUSPENSION SPREADER STOKER FIRING ARRANGEMENT FOR RDF

THE COMBUSTION PROCESS

In order to understand the formation of NOx in a solid waste combustion unit, it is first necessary to understand the combustion mechanism itself. In the combustion of solid waste, be it in a mass burn or Refuse Derived Fuel (RDF) type of combustion unit, certain steps take place. When the solid waste is first added to the furnace it has a moisture content of 20 to 30 percent. Minimal combustion takes place until this moisture is evaporated. Once the solid waste is dry, it continues to heat until the volatile compounds evolve and burn. The next step is the partial oxidation of the heavier organic compounds. These products burn with the volatilized compounds in the fire ball section. Some of the remaining solids will continue to burn in the solid phase.

The most widely used mechanism for burning RDF is the semi-suspension spreader stoker fuel burning system with a travelling grate similar to the type used in coal firing applications, but specially-designed for RDF. Figure 1 illustrates such an RDF burning system which is currently in use at facilities in Akron, Ohio; Niagara Falls, New York; East Hamilton, Ontario; Columbus, Ohio; Albany, New York; and Miami, Florida. The RDF distributor “throws” the RDF particles in a spread pattern into the furnace above the travelling grate which moves slowly back toward the distributor. The RDF particles burn partially in suspension above the grate, with completion of the combustion reaction on the grate. Underfire air is introduced under the grate and passes through the fuel bed. Overfire air is introduced above the grate to assure complete combustion.

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THEORY OF NOx FORMATION AND CONTROL

Nitrogen oxides are not inherently toxic or health endangering at concentrations below 15-20 ppm on a short-term basis (less than 6 hr) and 0.5 ppm long-term (up to a year). The National Ambient Air Quality Standard set by the USEPA is an annual average of 0.05 ppm (100 μg/m3). The more important problem with NOx emissions is their interaction with ozone and other photochemical oxidants in the atmosphere to form atmospheric smog.

Oxides of nitrogen occur naturally in the environment due to the reaction of atmospheric oxygen and nitrogen at equilibrium. Additional amounts of NOx are formed when any organic matter is burned with air because air is about 78 percent nitrogen (N2, by volume). Complete elimination of NOx is therefore impossible, even if nitrogen in the fuel is eliminated. The nitrogen content of municipal solid waste is typically between 0.5 and 0.1 percent by weight with a high degree of variability [2]. There is no practical way to “process out” the nitrogen in the solid waste because nitrogen is chemically bound in the organic compounds which make up the waste particles. There is, therefore, a theoretical lower limit for the formation of NOx below which emissions cannot drop, even utilizing all of the known techniques for NOx reduction. To be precise, the NOx formed within the flame is Nitrous Oxide (NO). It is not until the NO has exited the stack that the reaction proceeds from NO to NO2. Since both NO and NO2 are involved in the combustion process, the term “NOx” is used in this discussion. The air pollution control regulations dealing with NOx usually specify NO2 as the measured compound.

The research literature has a wealth of information about NOx formation from the combustion of gaseous and liquid fuels, and explains in detail the known mechanisms for the formation of NOx from the reaction of ambient N2 in a flame environment. The research which deals with the contribution of fuel-bound nitrogen to NOx emissions, however, is limited. Minimal study on NOx formation from the combustion of solid fuels exists,
and most research of this nature is based on laboratory-scale studies of pulverized coal combustion.

The following paragraphs summarize some of the results of research on the two contributors to NOₓ formation: atmospheric nitrogen (thermal NOₓ) and fuel nitrogen (fuel NOₓ).

**THERMAL NOₓ**

The NOₓ that is produced in the flame from the nitrogen present in ambient air is sometimes called "Thermal NOₓ" since it forms only at high temperatures.

The basic mechanism describing the formation of thermal NOₓ was first explained by Ya. Zeldovich in 1947 [3]. The basis of the Zeldovich mechanism is:

\[
O + N₂ = NO + N \\
N + O₂ = NO + O
\]

These reactions are interdependent with the first reaction determining the rate of reaction. Once this reaction is started, it is continuous. The rate of formation is exponentially dependent on temperature and is proportional to the square root of the oxygen concentration. Since the nitrogen concentration remains essentially constant during combustion, it is not an important factor.

Since the reaction is sensitive to both temperature and oxygen concentration, these are the first elements to be investigated for Thermal NOₓ control. Temperature sensitivity suggests that peak combustion temperatures should be avoided. Avoiding high heat release rates on the grate, thereby minimizing fuel bed temperature is one method for accomplishing this reduction. Another method is to limit the residence time of the fuel in peak combustion temperatures by "staging" the combustion as much as possible [4]. That is, the combustion should be controlled so that more partial oxidation of the fuel takes place in the hot fuel bed with completion of the combustion reaction in a cooler environment above the bed.

Sensitivity to oxygen concentration suggests that excess air should be minimized. The research of Pershing and Wendt [5] has shown that NOₓ formation decreases with a decreasing fuel-to-air ratio. This decrease continues until the ratio equals about 0.75 (or 133 percent of stoichiometric air). Below a ratio of 0.75 NOₓ formation increases.

**FUEL NOₓ**

The NOₓ which is formed by the oxidation of fuel-bound nitrogen during combustion is sometimes called
"fuel NO\textsubscript{x}." Research with liquid fuels indicates that the contribution of the fuel-bound nitrogen to NO\textsubscript{x} formation can be significant and is only slightly dependent on combustion temperature. NO\textsubscript{x} formation from fuel nitrogen in these experiments were mainly influenced by oxygen concentration \[6\]. Experiments with coal indicate that fuel NO\textsubscript{x} is the dominant mechanism for total NO\textsubscript{x} creation \[7\].

There is also evidence to suggest that fuel nitrogen conversion to NO\textsubscript{x} will be a greater factor in total NO\textsubscript{x} emissions from RDF combustion than from coal combustion. Experiments have shown a correlation between the fuel oxygen-to-nitrogen ratio and fuel nitrogen conversion to NO\textsubscript{x} with higher ratios correlating with higher NO\textsubscript{x} conversion \[8\]. Typical raw waste or RDF has a fuel oxygen-to-nitrogen ratio of between 20 and 30 as compared with typical coal values of between one and fifteen. Based on this higher ratio the research suggests that fuel nitrogen conversion in solid waste or RDF combustion will be about double that for coal combustion. Fig. 3 illustrates this phenomenon.

Significant work has been done by Y. H. Song of M.I.T. on NO\textsubscript{x} formation from solid fuel. In his most recent work, Song investigated NO\textsubscript{x} formation from fuel-bound nitrogen in pulverized coal combustion \[9\]. The experiments studied NO\textsubscript{x} formation from fuel-bound nitrogen by varying the fuel-to-air ratio and temperature. To eliminate the formation of thermal NO\textsubscript{x}, an artificial "air" was utilized which eliminated nitrogen from the mixture (79% helium, 21% oxygen).

The conclusions of the study are:

1. Changing combustion temperature alone does not have a very significant effect on fuel NO\textsubscript{x} emissions.

2. Fuel NO\textsubscript{x} emissions decrease very significantly with increasing fuel/oxygen equivalence ratio (decreasing excess air).

These conclusions suggest that to control fuel NO\textsubscript{x} contributions to total NO\textsubscript{x} emissions from a solid waste combustion unit, total excess air quantities should be kept at the lowest possible level without compromising carbon combustion efficiency (fuel burn-out). Song's experimental data suggest that fuel NO\textsubscript{x} contributions start to rise as the combustion air rises above 50 percent of stoichiometric. These conclusions suggest that underfire air should be kept at 50 to 75 percent of stoichiometric to keep the fuel bed in the starved oxygen mode with overfire air added above the grate to complete the combustion.

**COMBUSTION PROCESS NO\textsubscript{x} CONTROL**

The quantity of NO\textsubscript{x} dispersed to the atmosphere from a solid waste combustion unit can be reduced in two ways. The primary method is to control the reaction which produces the pollutant. As a second possibility, the pollutant might be removed after it is formed.

For resource recovery facilities, the most promising methods for NO\textsubscript{x} control are those involving the control of the combustion process itself. Wark and Warner \[4\] and several others \[6, 7\] have suggested certain reduction methods which are consistent with NO\textsubscript{x} formation theory. However, the research upon which these methods are based involves the combustion of coal, not solid waste. The results of NO\textsubscript{x} reduction techniques in coal combustion should be applied with caution to the combustion of raw solid waste or RDF. These control methods and their applicability to solid waste combustion are discussed in the following paragraphs.

**COMBUSTION ZONE COOLING AND BURNER CONFIGURATION**

The research indicates that cooling of the primary flame zone by heat transfer to surrounding surfaces should be maximized to keep the flame temperature to a minimum. Boiler designs utilizing waterwalls in the flame zone for convective and radiative cooling should accomplish the maximum amount of flame zone cooling. In addition, research indicates that highly turbulent burners with high heat release rates should be avoided. Furnace designs using moving grates for raw waste or spreader stokers and travelling grates inherently minimize heat release rates because the raw waste or RDF burns slowly on a large grate area as opposed to burning in a small, turbulent burner.
STAGED COMBUSTION

Two-stage combustion of coal in a two-chamber furnace has been tested and compared to a single-stage combustor. The results show impressive reductions in NOX [10]. Also, tests of the effects of varying amounts of overfire air in a tangentially-fired pulverized coal boiler show achievement of as much as 33 percent reduction of NOX emissions at 16 percent excess air [7]. Direct application of these results to solid waste combustion in general is, however, not possible. First, two-chamber combustion equipment exists only for small-scale mass burn applications which cannot be used efficiently for large facilities. Second, tangential burning of pulverized coal at 16 percent excess air is a completely different mechanism than the moving grate or travelling grate spreader stoker operating at 30 to 100 percent excess air. The literature shows that percent NOX reductions with overfire air adjustments are much lower (10 percent) at the higher excess air levels needed to burn raw waste or RDF. It can be concluded, nevertheless, that reductions in NOX may be achieved in either mass burn or RDF combustion units by providing additional levels of overfire air injection to accomplish partial staging of combustion.

FLUE GAS RECIRCULATION

Tests have been performed which demonstrate NOX emission reductions which can be achieved by recirculating as much as 20 percent of the flue gas back to the burners of a pulverized coal boiler [10]. The results show a 15-18 percent reduction in NOX formation. The primary effect of flue gas recirculation is a reduction in flame temperature by mixing the cooler flue gas with combustion air. In addition, oxygen concentration is reduced slightly.

Flue gas recirculation can be applied in solid waste combustion units by ducting cooled flue gas from a point after the air pollution control equipment back to the underfire air fan. Hirayama showed in a 1975 experiment in Japan [11] that a reduction of about 25 percent in the concentration of NOX in the flue gas could be achieved by recirculating flue gas exiting a spray scrubber back to the drying grates of a municipal solid waste incinerator at a ratio of 20 parts (by volume) flue gas and 80 parts fresh air. Furnace outlet temperatures ranged from 1290°F (700°C) to 1652°F (900°C).

This experiment suggests that this technique might be moderately successful in municipal solid waste energy recovery applications, however, the same effects of flue gas recirculation (i.e., lower flame temperature, and below stoichiometric underfire air) can probably be accomplished without flue gas recirculation. By designing the combustion unit properly to maintain moderate underfire air temperatures, and by careful operation of the boiler to keep underfire air amounts to 50-75 percent of stoichiometric, similar NOX reduction effects can be expected without the necessity to oversize all flue gas ducting and fans by 20 percent to allow for flue gas recirculation.

POST-COMBUSTION NOX CONTROL

Certain methods for controlling NOX emissions after formation in the combustion process have been tested and are being marketed. These methods fall into two general groups; (1) Selective Catalytic Reduction (SCR); and (2) Noncatalytic Reduction. Both involve mechanisms by which ammonia (NH3) is reacted with the NO in the flue gas.

SELECTIVE CATALYTIC REDUCTION (SCR)

SCR is a method of enhancing the NH3 + NO reaction which results in N2 and water. This reaction is very temperature dependent without a catalyst. SCR involves the use of a titanium oxide and vanadium oxide catalyst to enhance the NH3 + NO reaction. With SCR, the ammonia is injected into the flue gas stream at a point in which the flue gas is at a temperature of between 500°F and 800°F (260°C and 427°C). This is a much lower and wider temperature range than is required without the catalyst. The flue gas and ammonia mixture is introduced into the catalyst bed in which the NH3 reacts with the NO in the flue gas. The choice of V2O5 and TiO2 is almost universal among the available systems [12] because these catalyst materials are highly resistant to SO3 poisoning where Platinum or Paladium are not.

The SCR systems commercially available can achieve 80 percent removal of NO with essentially no NH3 slippage (or breakthrough). NH3 slippage occurs when ammonia travels through the catalyst bed without reacting. This phenomenon can cause the formation of ammonium sulfite or sulfate which can foul the air preheater and cause significant problems. In solid waste applications, ammonium chloride also can form due to the relatively high chlorine content in solid waste. Ammonium chloride is difficult to remove by any control device and has caused a visible plume when formed.

There are presently 62 full scale SCR processes presently in operation. Twenty-six of these are on units larger than 33 MW and seven are on units larger than 30 MW. All of the units are on oil or gas fired boilers with twenty five units exposed to SO2 and particulate. In the US, the first large scale SCR unit has been applied to half of Southern California Edison's Huntington Beach station.
which is a 215 MW gas and oil fired unit. This system is achieving 90 percent reduction of NO\textsubscript{X} at a cost of $10 million in capital and will use 40 tons (36,300 kg) per year of honeycomb catalyst and 320 tons (290,000 kg) per year of ammonia.

An SCR demonstration has been completed at Georgia Power Company's Plant Mitchell on a 0.5 MW slipstream [13, 14]. The system ran for 5,000 continuous hours and a total of 5620 hr before being removed due to the regular major maintenance schedule for the boiler. This system worked in the temperature range of 575°F to 750°F (302°C to 399°C). The results showed 80 percent NO removal with no NH\textsubscript{3} slippage and 90 percent NO removal with 40 ppm NH\textsubscript{3} slippage. The catalyst was V\textsubscript{2}O\textsubscript{5} and TiO\textsubscript{2} but the substrate was stainless steel wire mesh. This allowed for a lower pressure drop and less clogging by particulate.

For resource recovery facilities, SCR is a technique for the future. SCR has not been demonstrated on a solid waste combustion unit. The costs for the systems are not accurately known and the life expectancy of the catalyst is in doubt. When the catalyst is replaced, its cost can equal 50 percent of the capital cost of the SCR unit.

**NONCATALYTIC REDUCTION**

Ammonia can also be used to reduce NO without a catalyst being present. In this technique, NH\textsubscript{3} is injected into the furnace at a point in which the temperature is 1600-1650°F (871-899°C), an extremely narrow range. Within this temperature range the following reactions take place:

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

These reactions are very sensitive to temperature. Within the 1600-1600°F (871-899°C) window the NO\textsubscript{X} level will be reduced by 60 percent or more. At temperature above 1650°F (899°C) the NH\textsubscript{3} begins to oxidize to produce more NO\textsubscript{X}. If the temperature is below 1600°F (871°C), the reaction becomes so slow as to be ineffective.

There are potential problems with the use of ammonia injection on boilers burning municipal solid waste or RDF. The ammonia can react with other species found in the flue gas to produce NH\textsubscript{4}Cl, (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{3}, (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4}, etc. Each of these compounds can foul boiler preheaters and will cause a very visible plume. Acid gas scrubbing equipment will remove a part of these constituents but NH\textsubscript{4}Cl is particularly difficult to remove. A test of ammonia injection on a municipal incinerator has been performed in Japan on a unit which was also equipped with acid gas scrubbing equipment. The NO\textsubscript{X} was reduced by 60 percent, but a plume caused by ammonium chloride (NH\textsubscript{4}Cl) formation was visible for about five miles [15].

There has been very little experience with noncatalytic ammonia injection systems in units burning solid waste. It is not likely that these systems will achieve widespread use until more operating data and cost information is collected.

**SUMMARY AND CONCLUSIONS**

Because of a growing concern among regulators and citizen groups regarding NO\textsubscript{X} emissions, designers of resource recovery facilities must be aware of the available NO\textsubscript{X} control technology. This paper has reviewed NO\textsubscript{X} formation theory which suggests that NO\textsubscript{X} formed from fuel-bound nitrogen is most likely the dominant formation mechanism in solid waste combustion. This paper has also reviewed techniques to reduce NO\textsubscript{X} formation in the combustion process. The most effective of these techniques for solid waste combustion units are:

1. Design of the combustion unit to minimize grate heat release rates while still meeting the minimum solid waste burning capacity restrictions of the particular project.

2. Design of the combustion unit to include additional overfire air injection levels so that partial staging of the combustion can be accomplished by operating the unit with below stoichiometric under fire air.

3. Design of the combustion unit to include continuous monitoring of NO\textsubscript{X} emissions so that frequent adjustments of underfire air, bed temperature, and overfire air can be made to minimize NO\textsubscript{X} emissions.

This paper also reviewed the available techniques to eliminate NO\textsubscript{X} from the flue gas stream after the combustion process. Their application to solid waste combustion units has, however, been minimal and may introduce other air pollution problems.

**REFERENCES**


Key Words: Boiler • Combustion • Emission • Environment • Furnace • Gases • Performance • Pollution • Refuse • Refuse Derived Fuel • Spreader-Stoker • Stoker • Technology • Waterfall


INTRODUCTION

The present study is concerned with the optimization of a furnace to reduce emission of nitrogen oxide (NOx). Previous research has shown that NOx emissions are primarily the result of the combustion process. To understand the mechanism of NOx formation, it is necessary to study the interactions between fuel, air, and temperature. The purpose of this study is to investigate the factors affecting NOx formation in a pulverized coal-fired furnace.