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EMISSION

EMISSIONS

POLLUTANTS AND CONTROL TECHNIQUES

Combustion of standard fossil fuels (natural gas and Oil) in commercial and industrial boilers results in the following nine emissions; carbon dioxide, nitrogen, oxygen, water, carbon monoxide, nitrogen oxide, sulfur oxides, volatile organic compounds, and particulate matter. The latter five products of combustion are considered pollutants and are known to, either directly or indirectly, cause harmful affects on humans and the environment. The following section describes the formation and control of each of the pollutants in commercial and industrial boilers:

- Carbon Monoxide
- Nitrogen Oxides
- Sulfur Oxides
- Volatile Organic Compounds/Hydrocarbons
- Particulate Matter

NITROGEN COMPOUNDS (NO_x)

Although there is evidence proving NO_x, in itself, is harmful to humans, the main reason NO_x is considered an environmental problem is because it initiates reactions that result in the production of ozone and acid rain. Ozone and acid rain can damage fabric, cause rubber to crack, reduce visibility, damage buildings, harm forests and lakes, and cause health problems. By controlling NO_x levels, along with the other pollutants, the levels of acid rain and ozone can be reduced.

The principal nitrogen pollutants generated by boilers are nitric oxide (NO) and nitrogen dioxide (NO₂), collectively referred to as NO_x. The contribution from different NO_x sources to the total NO_x levels varies among metropolitan areas. In general, the contribution of mobile sources to the total NO_x level ranges from 60 to 80 percent: For stationary sources, it ranges between 20 and 40 percent. A significant portion of the NO_x from stationary sources can be attributed to residential, commercial, and industrial sources, including industrial boilers. In industrial boilers, NO_x is primarily formed in two ways; thermal NO_x and fuel NO_x: Thermal NO_x is formed when nitrogen and oxygen in the combustion air combine with one another at the high temperatures in a flame. Thermal NO_x makes up the majority of NO_x formed during the combustion of gases and light oils.

Fuel NO_x is formed by the reaction of nitrogen in the fuel with oxygen in the combustion air. It is rarely a problem with gaseous fuels. But in oils containing significant amounts of fuel-bound nitrogen, fuel NO_x can account for up to 50% of the total NO_x emissions. NO_x emissions from boilers are influenced by many factors. The most significant factors are flame temperature and the amount of nitrogen in the fuel. Other factors affecting NO_x formation are excess air level and combustion air temperature.

While flame temperature primarily affects thermal NO_x formation, the amount of nitrogen in the fuel determines the level of fuel NO_x emissions. Fuel containing more nitrogen results in higher levels of NO_x emissions. Most NO_x control technologies for industrial boilers, with inputs less than 100 MMBtu/hr, reduce thermal NO_x and have little affect on fuel NO_x. Fuel NO_x is most economically reduced in commercial and industrial boilers by switching to cleaner fuels (fuels containing less fuel-bound nitrogen), if available.

NO_x CONTROL TECHNOLOGIES

NO_x controls can be classified into two types: post combustion methods and combustion control techniques. Post combustion methods address NO_x emissions after formation while combustion control techniques prevent the formation of NO_x during the combustion process. Post combustion methods tend to be more expensive than combustion control techniques and generally are not used on boilers with inputs of less than 100 MMBtu/hr. Following is a list of different NO_x control methods.

Post combustion control methods include:

- Selective Non-Catalytic Reduction
- Selective Catalytic Reduction

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Combustion control techniques include:

- Low Excess Air Firing
- Low Nitrogen Fuel Oil
- Burner Modifications
- Water/Steam Injection
- Flue Gas Recirculation

Each method results in a different degree of NO_x control. For example, when firing natural gas, low excess air firing typically reduces NO_x by 10%, flue gas recirculation by 75%, and selective catalytic reduction by 90%.

POST COMBUSTION CONTROL METHODS

Selective Non-catalytic Reduction

Selective non-catalytic reduction involves the injection of a NO_x reducing agent, such as ammonia or urea, into the boiler exhaust gases at a temperature of approximately 760-870 °C. The ammonia or urea breaks down the NO_x in the exhaust gases into water and atmospheric nitrogen. Selective non-catalytic reduction reduces NO_x up to 70%.

However, the technology is extremely difficult to apply to industrial boilers that modulate or cycle frequently. This is because the ammonia (or urea) must be injected in the flue gases at a specific flue gas temperature. And, in industrial boilers that modulate or cycle frequently, the location of the exhaust gases at the specified temperature is constantly changing. Thus, it is not feasible to apply selective non-catalytic reduction to industrial boilers that have high turndown capabilities and modulate or cycle frequently.

Selective Catalytic Reduction

Selective catalytic reduction involves the injection of ammonia in the boiler exhaust gases in the presence of a catalyst. The catalyst allows the ammonia to reduce NO_x levels at lower exhaust temperatures than selective non-catalytic reduction. Unlike selective non-catalytic reduction, where the exhaust gases must be approximately 760-870 °C selective catalytic reduction can be utilized where exhaust gasses are between 260 °C and 650 °C, depending on the catalyst used. Selective catalytic reduction can result in NO_x reductions up to 90%. However, it is costly to use and can rarely be cost justified on boilers with inputs less than 100 MMBtu/hr.

COMBUSTION CONTROL TECHNIQUES

Combustion control techniques reduce the amount of NO_x emission by limiting the amount of NO_x formation during the combustion process. This is typically accomplished by lowering flame temperatures. Combustion control techniques are more economical than post combustion methods and are frequently utilized on industrial boilers requiring NO_x controls.

Low Excess Air (LEA) Firing

As a safety factor to assure complete combustion, boilers are fired with excess air. One of the factors influencing NO_x formation in a boiler is the excess air levels. High excess air levels (>45%) may result in increased NO_x formation because the excess nitrogen and oxygen in the combustion air entering the flame will combine to form thermal NO_x. Low excess air firing involves limiting the amount of excess air that is entering the combustion process in order to limit the amount of extra nitrogen and oxygen that enters the flame. Limiting the amount of excess air entering a flame is accomplished through burner design and can be optimized through the use of oxygen trim controls. Low excess air firing can be used on most boilers and generally results in overall NO_x reductions of 5-10% when firing natural gas.

Low Nitrogen Fuel Oil

When firing fuel oils, NO_x formed by fuel-bound nitrogen can account for 20-50% of the total NO_x level. One method to reduce NO_x levels from boilers firing distillate oils is through the use of low nitrogen fuel oil. Low nitrogen oils can contain up to 15-20 times less fuel-bound nitrogen than standard No. 2 oil (less than 0.001% fuel-bound nitrogen). When low NO_x oil is fired in firetube boilers utilizing flue gas recirculation, NO_x reductions of 60%-70% over NO_x emissions from standard No. 2 oils have been achieved. Burner modifications for NO_x control involve changing the design of a standard burner in order to create a larger flame. Enlarging the flame results in lower flame temperatures and lower thermal NO_x formation which, in turn, results in lower overall NO_x emissions. The technology can be applied to most boiler types and sizes. It is most effective when firing natural gas and distillate fuel oil and has little affect on boilers firing heavy oil. To comply with the more stringent regulations, burner modifications must be used in conjunction with other NO_x reduction methods, such

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as flue gas recirculation. If burner modifications are utilized exclusively to achieve low NO_x levels (30 ppm), adverse affects on boiler operating parameters such as turndown, capacity, CO levels, and efficiency may result. It is important to address all aspects of boiler performance when selecting NO_x control technologies.

Water/Steam Injection

Water or steam injection can be utilized to reduce NO_x levels. By injecting water or steam into the flame, flame temperatures are reduced, thereby lowering thermal NO_x formation and overall NO_x levels. Water or steam injection can reduce NO_x up to 80% (when firing natural gas) and can result in lower reductions when firing oils. There is a practical limit to the amount of water or steam that can be injected into the flame before condensation problems are experienced. Additionally, under normal operating conditions, water/steam injection can result in a 3-10% boiler efficiency loss. Many times water or steam injection is used in conjunction with other NO_x control methods such as burner modifications or flue gas recirculation.

Flue Gas Recirculation

Flue gas recirculation, or FGR, is the most effective method of reducing NO_x emission from industrial boilers with inputs below 100 MMBtu/hr. FGR entails recirculating a portion of relatively cool exhaust gases back into the combustion process in order to lower the flame temperature and reduce NO_x formation. It is currently the most effective and popular low NO_x technology for firetube and watertube boilers. And, in many applications, it does not require any additional reduction equipment to comply with regulations.

Flue gas recirculation technology can be classified into two types; external or induced.

- External flue gas recirculation utilizes an external fan to recirculate the flue gases back into the flame. External piping routes the exhaust gases from the stack to the burner. A valve controls the recirculation rate, based on boiler input.
- Induced flue gas recirculation utilizes the combustion air fan to recirculate the flue gases back into the flame. A portion of the flue gases are routed by duct work or internally to the combustion air fan, where they are premixed with the combustion air and introduced into the flame through the burner. New designs of induced FGR that utilize an integral FGR design are becoming popular among boiler owners and operators because of their uncomplicated design and reliability.

Theoretically, there is no limit to the amount of NO_x reduction with FGR; practically, there is a physical, feasible limit. The limit of NO_x reduction varies for different fuels ~ 80% for natural gas and 20-25% for standard fuel oils.

The current trends with low NO_x technologies are to design the boiler and low NO_x equipment as a package. Designing as a true package allows the NO_x control technology to be specifically tailored to match the boiler's furnace design features, such as shape, volume, and heat release. By designing the low NO_x technology as a package with the boiler, the adverse effects of the low NO_x technology on boiler operating parameters (turndown, capacity, efficiency, and CO levels) can be addressed and minimized.

CHOOSING THE BEST NO_x TECHNOLOGY FOR THE JOB

What effect does NO_x control technology ultimately have on a boiler's performance? Certain NO_x controls can worsen boiler performance while other controls can appreciably improve performance. Aspects of the boiler performance that could be affected include turndown, capacity, efficiency, excess air, and CO emissions.

Failure to take into account all of the boiler operating parameters can lead to increased operating and maintenance costs, loss of efficiency, elevated CO levels, and shortening of the boiler's life.

The following section discusses each of the operating parameters of a boiler and how they are related to NO_x control technologies.

Turndown

Choosing a low NO_x technology that sacrifices turndown can have many adverse effects on the boiler. When selecting NO_x controls, the boiler should have a turndown capability of at least 4:1 or more, in order to reduce operating costs and the number of on/off cycles. A boiler utilizing a standard burner with a 4:1 turndown can cycle as frequently as 12 times per hour or 288 times a day because the boiler must begin to cycle at inputs below 25% capacity.

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With each cycle, pre- and post-purge air flow removes heat from the boiler and sends it out the stack. The energy loss can be reduced by using a high turndown burner (10:1), which keeps the boiler on even at low firing rates.

Every time the boiler cycles off, before it comes back on, it must go through a specific start-up sequence for safety assurance. It takes between one to two minutes to get the boiler back on line. If there is a sudden load demand, the response cannot be accelerated. Keeping the boiler on line assures a quick response to load changes.

Frequent cycling also deteriorates the boiler components. The need for maintenance increases, the chance of component failure increases, and boiler downtime increases. So, when selecting NO_x control, always consider the burners turndown capability.

Capacity

When selecting the best NO_x control, capacity and turndown should be considered together because some NO_x control technologies require boiler derating in order to achieve guaranteed NO_x reductions. For example, flame shaping (primarily enlarging the flame to produce a lower flame temperature - thus lower NO_x levels) can require boiler derating, because the shaped flame could impinge on the furnace walls at higher firing rates.

However, the boiler's capacity requirement is typically determined by the maximum load in the steam/hot water system. Therefore, the boiler may be oversized for the typical load conditions that may occur. If the boiler is oversized, its ability to handle minimum loads without cycling is limited. Therefore, when selecting the most appropriate NO_x control, capacity and turndown should be considered together for proper boiler selection and to meet overall system load requirements.

Efficiency

Some low NO_x controls reduce emissions by lowering flame temperature, particularly in boilers with inputs less than 100 MMBtu/hr. Reducing the flame temperature decreases the radiant heat transfer from the flame and could lower boiler efficiency. The efficiency loss due to the lower flame temperatures can be partially offset by utilizing external components, such as an economizer. Or, the offset technique can be inherent in the NO_x design.

One technology that offsets the efficiency loss due to lower flame temperatures in a firetube boiler is flue gas recirculation. Although the loss of radiant heat transfer could result in an efficiency loss, the recirculated flue gases increase the mass flow through the boiler - thus the convective heat transfer in the tube passes increases. The increase in convective heat transfer compensates for losses in radiant heat transfer, with no net efficiency loss. When considering NO_x control technology, remember, it is not necessary to sacrifice efficiency for NO_x reductions. Excess Air A boiler's excess air supply provides for safe operation above stoichiometric conditions. A typical burner is usually set up with 10-20% excess air (2-4% O₂). NO_x controls that require higher excess air levels can result in fuel being used to heat the air rather than transferring it to usable energy. Thus, increased stack losses and reduced boiler efficiency occur. NO_x controls that require reduced excess air levels can result in an oxygen deficient flame and increased levels of carbon monoxide or unburned hydrocarbons. It is best to select a NO_x control technology that has little effect on excess air.

Carbon Monoxide (CO) Emissions

High flame temperatures and intimate air/fuel mixing are essential for low CO emissions. Some NO_x control technologies used on industrial and commercial boilers reduce NO_x levels by lowering flame temperatures by modifying air/fuel mixing patterns. The lower flame temperature and decreased mixing intensity can result in higher CO levels.

An induced flue gas recirculation package can lower NO_x levels by reducing flame temperature without increasing CO levels. CO levels remain constant or are lowered because the flue gas is introduced into the flame in early stages of combustion and the air fuel mixing is intensified. Intensified mixing offsets the decrease in flame temperature and results in CO levels that are lower than achieved without FGR. But, the level of CO depends on the burner design. Not all flue gas recirculation applications result in lower CO levels.

Total Performance

Selecting the best low NO_x control package should be made with total boiler performance in mind. Consider the application. Investigate all of the characteristics of the control technology and the effects of the technology on the boiler's performance. A NO_x control technology that results in the greatest NO_x reduction is not necessarily the best for the application or the best for high turndown, adequate capacity, high efficiency, sufficient excess

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air, or lower CO. The newer low NO_x technologies provide NO_x reductions without affecting total boiler performance.

SULFUR COMPOUNDS (SO_x)

The primary reason sulfur compounds, or SO_x, are classified as a pollutant is because they react with water vapor (in the flue gas and atmosphere) to form sulfuric acid mist. Airborne sulfuric acid has been found in fog, smog, acid rain, and snow. Sulfuric acid has also been found in lakes, rivers, and soil. The acid is extremely corrosive and harmful to the environment.

The combustion of fuels containing sulfur (primarily oils and coals) results in pollutants occurring in the forms of SO₂ (sulfur dioxide) and SO₃ (sulfur trioxide), together referred to as SO_x (sulfur oxides). The level of SO_x emitted depends directly on the sulfur content of the fuel. The level of SO_x emissions is not dependent on boiler size or burner design. Typically, about 95% of the sulfur in the fuel will be emitted as SO₂, 1-5% as SO₃, and 1-3% as sulfate particulate. Sulfate particulate is not considered part of the total SO_x emissions.

Historically, SO_x pollution has been controlled by either dispersion or reduction. Dispersion involves the utilization of a tall stack, which enables the release of pollutants high above the ground and over any surrounding buildings, mountains, or hills, in order to limit ground level SO_x emissions. Today, dispersion alone is not enough to meet more stringent SO_x emission requirements; reduction methods must also be employed.

Methods of SO_x reduction include switching to low sulfur fuel, desulfurizing the fuel, and utilizing a flue gas desulfurization (FGD) system. Fuel desulfurization, which primarily applies to coal, involves removing sulfur from the fuel prior to burning. Flue gas desulfurization involves the utilization of scrubbers to remove SO_x emissions from the flue gases.

Flue gas desulfurization systems are classified as either non-regenerable or regenerable. Non-regenerable FGD systems, the most common type, result in a waste product that requires proper disposal. Regenerable FGD converts the waste by-product into a marketable product, such as sulfur or sulfuric acid. SO_x emission reductions of 90-95% can be achieved through FGD. Fuel desulfurization and FGD are primarily used for reducing SO_x emissions for large utility boilers. Generally the technology cannot be cost justified on industrial boilers.

For users of industrial boilers, utilizing low sulfur fuels is the most cost effective method of SO_x reduction. Because SO_x emissions primarily depend on the sulfur content of the fuel, burning fuels containing a minimal amount of sulfur (distillate oil) can achieve SO_x reductions, without the need to install and maintain expensive equipment.

CARBON MONOXIDE (CO)

Carbon monoxide is a pollutant that is readily absorbed in the body and can impair the oxygen-carrying capacity of the hemoglobin. Impairment of the body's hemoglobin results in less oxygen to the brain, heart, and tissues. Even short-term over exposure to carbon monoxide can be critical, or fatal, to people with heart and lung diseases. It may also cause headaches and dizziness in healthy people.

During combustion, carbon in the fuel oxidizes through a series of reactions to form carbon dioxide (CO₂). However, 100 percent conversion of carbon to CO₂ is rarely achieved in practice and some carbon only oxidizes to the intermediate step, carbon monoxide.

Older boilers generally have higher levels of CO than new equipment because CO has only recently become a concern and older burners were not designed to achieve low CO levels. In today's equipment, high levels of carbon monoxide emissions primarily result from incomplete combustion due to poor burner design or firing conditions (for example, an improper air-to-fuel ratio) or possibly a leaky furnace. Through proper burner maintenance, inspections, operation, or by upgrading equipment or utilizing an oxygen control package, the formation of carbon monoxide can be controlled at an acceptable level.

PARTICULATE MATTER (PM)

Emissions of particulate matter (PM) from combustion sources consist of many different types of compounds, including nitrates, sulfates, carbons, oxides, and any uncombusted elements in the fuel. Particulate pollutants can be corrosive, toxic to plants and animals, and harmful to humans.

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Particulate matter emissions generally are classified into two categories, PM and PM10. PM10 is a particulate matter with a diameter less than 10 microns. All particulate matter can pose a health problem. However, the greatest concern is with PM10, because of its ability to bypass the body's natural filtering system.

PM emissions are primarily dependent on the grade of fuel fired in the boiler. Generally, PM levels from natural gas are significantly lower than those of oils. Distillate oils result in much lower particulate emissions than residual oils.

When burning heavy oils, particulate levels mainly depend on four fuel constituents: sulfur, ash, carbon residue, and asphalenes. These constituents exist in fuel oils, particularly residual oils, and have a major effect on particulate emissions. By knowing the fuel constituent levels, the particulate emissions for the oil can be estimated.

Methods of particulate control vary for different types and sizes of boilers. For utility boilers, electrostatic precipitators, scrubbers, and baghouses are commonly utilized. For industrial and commercial boilers, the most effective method is to utilize clean fuels. The emission levels of particulate matter can be lowered by switching from a residual to a distillate oil or by switching from a distillate oil to a natural gas. Additionally, through proper burner set-up, adjustment and maintenance, particulate emissions can be minimized, but not to the extent accomplished by switching fuels.

VOLATILE ORGANIC COMPOUNDS (VOCs)/HYDROCARBONS (HC)

Volatile organic compounds, or VOCs, are compounds containing combinations of carbon, hydrogen, and sometimes oxygen. VOCs vaporize easily once emitted into the air and are of concern because of their role in ground level ozone formation. In reference to boiler performance, they are often referred to as hydrocarbons and generally are divided into two categories - methane and non-methane. Formation of VOCs in commercial and industrial boilers primarily result from poor or incomplete combustion due to improper burner set-up and adjustment. To control VOC emissions from commercial and industrial boilers, no auxiliary equipment is needed; properly maintaining the burner/boiler package will keep VOC emissions at a minimum. Proper maintenance includes keeping the air/fuel ratio at the manufacturer's specified setting, having the proper air and fuel pressures at the burner, and maintaining the atomizing air pressure on oil burners at the correct levels. An improperly maintained boiler/burner package can result in VOC levels over 100 times the normal levels.

EMISSION LEVEL UNITS

This section describes the different units for emission levels. Emission levels can be provided in many different units depending on whether the measurement is volume or mass based.

CORRECTING EMISSIONS TO 3% OXYGEN (15% EXCESS AIR)

The following equation shows how to correct emission readings to 3% oxygen (15% excess air). Because boilers don't always operate at 3% oxygen, it is necessary to convert ppm values measured at various excess air levels to 3% oxygen for comparison and regulation compliance purposes. To correct emission levels to 3% oxygen that are referenced to excess air levels other than 3%, use the following equation.

$$\text{ppm}(@ 3\%) = \left(\frac{21-3}{21-\text{O}_2(\text{actual})} \right) \text{ppm}(\text{actual})$$

Example: What is the NO_x level corrected to 3% oxygen for a measured level of 27 ppm at 7.1% oxygen?

$$\text{ppm}(@ 3\%) = \left(\frac{21-3}{21-7.1} \right) 27 = 35\text{ppmNO}_x$$

CONVERTING EMISSIONS BETWEEN PPM AND LB/MMBTU

Although emission levels can be given in many different units, the most common are ppm (corrected to 3% oxygen) and lb/MMBtu. Conversion between these two types of units is very simple, however, it does depend on the fuel type and excess air level.

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CALCULATION OF ANNUAL EMISSIONS FOR INDUSTRIAL BOILERS

When addressing industrial boilers, the potential annual emissions of NO_x are of concern and frequently must be calculated. Following is an example of how to calculate the potential annual NO_x emissions for industrial boilers.

To determine the annual NO_x emissions for an industrial boiler, three items must be known:

1. The NO_x emission factor for the boiler.
2. The maximum rated input for the boiler.
3. The maximum allowable hours of operation for the boiler.

Once the information above is obtained, the following equation can be used to determine annual emissions.

Emission Factor x Boiler Input x Annual Hours of Operation = Total Annual Emissions

For example, the calculation of the total annual NO_x emissions for an 800 hp boiler operating 24 hours/day, 365 days/year and having a NO_x level of 110 ppm would be as follows.

- Emission Factor = 0.13 lb/MMBtu (110 ppm = 0.13 lb/MMBtu)
- Boiler Input = 33.5 MMBtu/hr (Based on 80% Efficiency)
- Annual Hours of Operation = 8760 hours/year (24 hours/day x 365 days/year)

Substituting this data into the previous equation yields the annual NO_x emissions for this specific boiler, which is 19.1 tpy.