NOx BARCT Analysis Review

South Coast Air Quality Management District (SCAQMD)

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Prepared by: R. S. Todd, E. Lin, J. Zhang, C. A. Steves, J. P. Norton
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1. Introduction

The SCAQMD (South Coast Air Quality Management District) is reviewing the Best Available Retrofit Control Technologies (BARCT) for stationary emitters of nitrogen oxides (NOx) from refineries in the Los Angeles area. The outcome of this review will set NOx emission limits for refinery equipment in the District. As part of the assessment, the SCAQMD is looking for an independent third party review of the cost estimate and technology selections for equipment categories that are currently in the SCAQMD's RECLAIM (REgional CLean Air Incentives Market) Program. These NOx BARCT emission limits will be incorporated into proposed Rule 1109.1, NOx Emission Reductions for Refinery Equipment.

Norton Engineering Consultants (NEC) was commissioned to review the available and emerging technologies used in the refining sector to control NOx emissions. NEC has over 25 years of experience working with clients in the refining sector identifying and implementing NOx control technologies across a wide range of fired equipment. Based on field experience and vendor feedback, NEC have reviewed the Districts initial findings and provided commentary on the applicable NOx control technologies. The equipment categories that have been identified by the SCAQMD include:

(a) Heaters and boilers:

- (i) Process heaters,
- (ii) Boilers,
- (iii) SMR (Steam Methane Reformers) heaters,
- (iv) Sulfuric Acid Plant furnaces.

(b) Other categories:

- (v) FCCU (Fluid Catalytic Cracking Units),
- (vi) Gas turbines (with and without duct burners),
- (vii) Coke Calciner,
- (viii) Sulfur Recovery Unit Tail Gas (SRU TG) incinerators, flares and thermal oxidizers.

This report summarizes the findings and commentary from NEC's review of the available NOx control technologies proposed for each equipment category under proposed Rule 1109.1. NECs scope of work in this study is limited to an assessment of the available NOx control technologies. A separate review is underway by FERCo to assess and evaluate the challenges, constraints, and associated cost of control technology installations at large facilities.

2. Mechanisms of NOx Formation

Although several oxides of nitrogen are known to exist, the combustion zone of a typical refinery heater, boiler and incinerator will produce NO, along with smaller amounts (less than 5%) of NO_2. Therefore, in the context of this report, NOx will be primarily associated with NO. There are three (3) pathways that lead to NOx formation in a combustion process.

2.1 Thermal NOx

The reaction between molecular N_2 and O_2 at elevated temperature produces Thermal NOx.

$$N_2 + O_2 \xrightarrow{high\ temperature} 2\ NO$$

$$N_2 + 2\ O_2 \xrightarrow{high\ temperature} 2\ NO_2$$

The parameters that influence Thermal NOx formation are:

(a) The temperature of N_2 and O_2,

(b) The concentration of N_2 and O_2, and

(c) The residence time N_2 and O_2 spend together at elevated temperature.

As the air-to-fuel ratio increases in a combustion process, Thermal NOx formation increases until a maxima is reached. Further increases in the air-to-fuel ratio beyond this maxima reduces Thermal NOx formation due to the cooling effect of excess air in the flue gas. The Zeldovich mechanism relates the dissociation of N_2 and O_2 with the formation of NOx and observations show the formation rate:[1]

(i) Increases exponentially with increasing temperature.

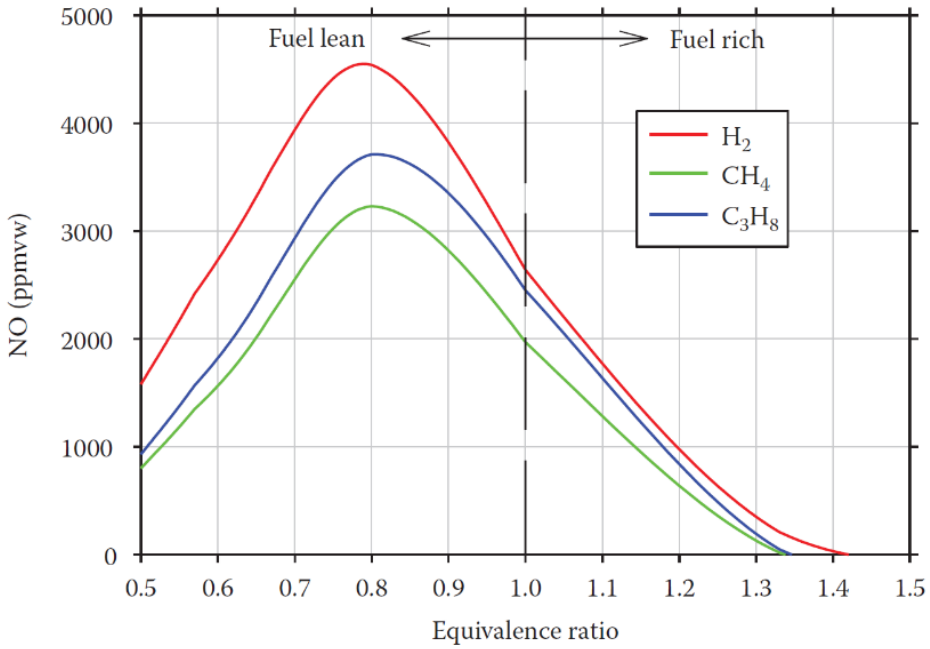
(ii) Increases linearly with increasing residence time.

For long residence times equilibrium dictates the formation of Thermal NOx, see Figure 2.1-1. However, a typical refinery heater rarely achieves these equilibrium levels in the flue gas. Cold plane surface area that can "see" the combustion zone rapidly cools the products of combustion via radiant heat transfer. As a result, N_2 and O_2 spend a very short amount of time at elevated temperature in the flame front before the combustion products radiate heat to the available cold plane surface area.

Residence times are typically short in a refinery heater so the techniques employed to minimize Thermal NOx formation are focused on reducing peak flame temperature and controlling reactant concentrations, primarily O_2, in the flame front.

[1] C. E. Baukal Jr (editor) "The John Zink Hamworthy Combustion Handbook", Second Edition, Volume 1 – Fundamentals, Chapter 15: NOx Emissions, 2013, Taylor & Francis Group, LLC

Figure 2.1-1: Adiabatic equilibrium Thermal NOx as a function of equivalence ratio (inverse stoichiometric ratio) for the combustion of various fuels (Source: Figure 15.7 from Baukal)[1]



2.2 Prompt NOx

The reaction pathway to Prompt NOx involves the attack of N_2 from hydrocarbon radicals formed in the combustion zone, which generates precursor species that in turn react with O_2 to form NO. Prompt NOx has been observed under fuel-rich combustion conditions at the flame front with hydrocarbon as the fuel (Prompt NOx was not observed in CO or H_2 flames) and was found to be relatively insensitive to flame temperature.[2] The kinetics of Prompt NOx formation are very fast and are most prevalent during the early stages of combustion, hence the term "Prompt".

Prompt NOx is a small contributor to the overall rate of NOx formation as it occurs under fuel-rich combustion conditions where NOx emissions are typically low.[3] In a fired heater or boiler, Prompt NOx may be a consideration when staged combustion is performed under fuel-rich conditions. In general, however, Prompt NOx is a small contributor to the overall rate of NOx formation and will be a function of the burner and/or combustor design.

[2] C.P. Fenimore "Formation of nitric oxide in premixed hydrocarbon flames", Thirteenth Symposium (International) on Combustion, vol. 13, 1971, pp 373 – 380.

[3] US EPA Office of Air Quality Planning and Standards "Alternative Control Techniques Document - NOx Emissions from Process Heaters (Revised)", 1993, EPA-453/R-93-034

2.3 Fuel NOx

Fuel NOx is generated when N-bound molecules in the fuel that are not N_2, often referred to as "precursor species", are burned in a combustion zone.

$$C_xH_yN + (\tfrac{1}{2} + x + \tfrac{1}{4}y)\,O_2 \xrightarrow{high\ temperature} NO + x\,CO_2 + \tfrac{1}{2}y\,H_2O$$

$$C_xH_yN + (1 + x + \tfrac{1}{4}y)\,O_2 \xrightarrow{high\ temperature} NO_2 + x\,CO_2 + \tfrac{1}{2}y\,H_2O$$

Fuel NOx is common when burning coal and heavy fuel oil which contain organic precursor species. However, gaseous fuels typically do not contain precursor species and most installations in a refinery burn Natural Gas (NG) and/or Refinery Fuel Gas (RFG), which are not a significant source of Fuel NOx.[1]

One source of Fuel NOx in the refinery is the waste gas stream entering the combustor in a Claus Plant (Sulfur Recovery Unit), this fuel source generally contains NH_3 and HCN.

In general, reducing peak flame temperature in the combustion zone is one of the few options available to reduce the conversion of precursor species to Fuel NOx.

2.3.1 NOx from a Fluid Catalytic Cracking Unit (FCCU)

Some of the nitrogen containing species present in the hydrocarbon feed to the FCCU end up in the coke on the catalyst. When the coke is burned off the catalyst in the regenerator, the nitrogen-bound species are liberated, forming precursor species and N_2. Around half of the nitrogen in the feed ends up in the coke and between 10 and 30% of the nitrogen-bound species in the coke will form precursor species, NH_3 and HCN, as they burn off the catalyst.[4] The fate of these precursor species in the FCCU regenerator depends on the operating conditions.

In full burn mode there is excess oxygen present and the precursor species burn out to form NOx or N_2 depending on the air/catalyst mixing conditions in the fluidized bed and operating temperature.

If the FCCU regenerator is operating in partial burn mode then precursor species are not burned out and remain in the flue gas leaving the regenerator. Partial burn mode operation is also characterized by high CO concentrations in the flue gas which is burned out in a downstream CO Boiler. The presence of precursor species entering the combustor of the CO Boiler means Fuel NOx is a large contributor to the overall NOx emissions from the CO Boiler.

Operating temperature in the FCCU regenerator does not exceed 1,500°F and the resulting amount of Thermal NOx is insignificant. Therefore, the total output of NOx from the FCCU regenerator (plus CO Boiler when operating in partial burn mode) is a complex function of the operating conditions that lead to Fuel NOx formation and the specific regenerator design.

[4] R. G. Kunz "Environmental Calculations: A Multimedia Approach", Appendix J: Air Pollution Aspects of the Fluid Catalytic Cracking Process, 2009, John Wiley & Sons, Inc.

3. NOx Control Technologies

Based on discussions from the previous section, Thermal NOx is the primary source of NOx that is emitted from a fired heater or boiler. Precursor species are rarely present in the fuel. Fuel NOx is a consideration when burning the coke off the catalyst in a FCCU regenerator or waste gas destruction in the combustor of a Claus Plant. Prompt NOx is not expected to be an important mechanism in the overall formation of NOx but may become a contributor when designing burners and/or combustors for very low NOx numbers under fuel-rich conditions with staged fuel combustion.

Three categories are available to reduce NOx emissions from the originating source in a refinery.

(a) *Remove N Species:* N_2 in the combustion zone produces Thermal NOx so removing N_2 from the oxidant takes away one of the primary reactants.

(b) *NOx Control at the Point of Generation:* Thermal NOx formation is influenced by temperature, reactant concentrations and residence time and manipulating these parameters can influence the formation of NOx at the point of generation, the combustion zone.

(c) *End of Pipe Solution:* Thermal NOx is uncontrolled in the combustion zone and downstream processing units selectively remove NOx from the flue gas.

Removing N_2 from combustion air is not a practical solution in a refinery setting. Large volumes of O_2 would be required that necessitates the installation of a dedicated cryogenic air separation plant along with an extensive distribution network to get O_2 to each combustion zone. Another complicating factor is enriched-O_2 combustion technologies are not commonly used in the refinery and would require a significant upgrade of the existing infrastructure and a reassessment of operating/safety procedures. Therefore, option (a) to remove N_2 from the feedstock to a combustion process should not be a consideration under proposed Rule 1109.1.

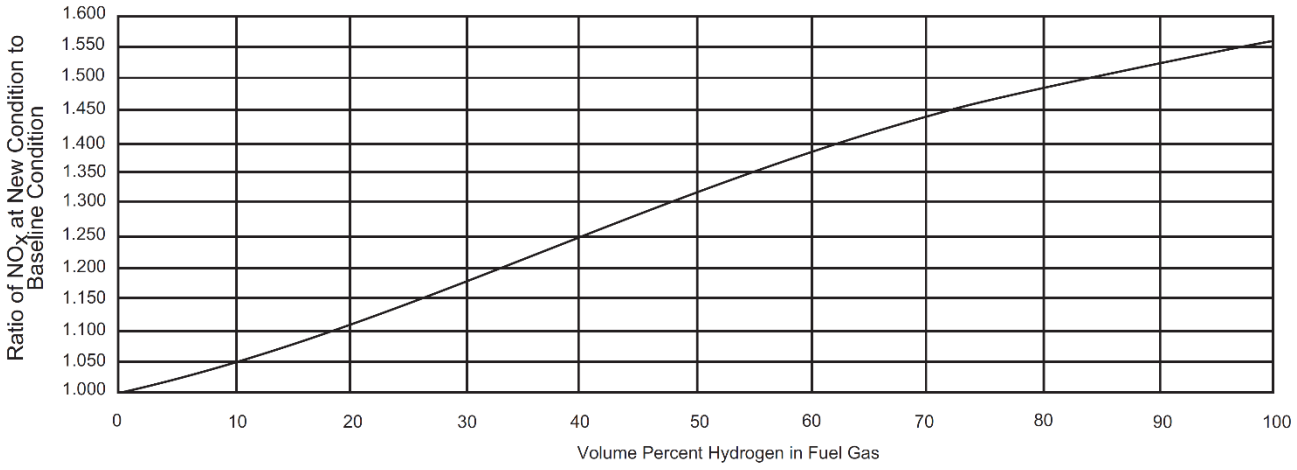
This leaves (b) NOx Control at the Point of Generation and (c) End of Pipe Solution as the methods available to reduce NOx emissions from a refinery. In some cases a combination of (b) and (c) may be implemented to reach the NOx BARCT limit. These two categories will be reviewed independently before assessing each individual NOx emitter within the refinery.

3.1 NOx Control at the Point of Generation

3.1.1 Fuel Switching

Refinery Fuel Gas (RFG) is a gaseous mixture of methane, light hydrocarbons and hydrogen along with smaller amounts of other miscellaneous species that is a common source of fuel used in most refinery heaters and boilers. RFG is the light end by-product from several processing units including catalytic reforming, hydrotreating, hydrocracking, catalytic cracking and coking.[5] H_2 content in RFG typically swings between 10 and 60 vol% based on variabilities in the operating conditions of the source providers. NOx emissions increase when combusting elevated levels of H_2 and olefins in the fuel gas as these components burn hotter than paraffinic components. The impact of fuel H_2 content versus NOx formation is shown in Figure 3.1-1.[6] The basis of Figure 3.1-1 assumes the composition of the fuel that is not hydrogen does not change. Removing H_2 and olefins from the fuel reduces peak flame temperature and reduces Thermal NOx formation. Natural Gas (NG, which is primarily methane) is an alternative fuel that is currently used in the refinery, typically for pilot burner fuel and to supplement refinery fuel gas, and is hydrogen and olefin free.

Figure 3.1-1: Impact of H_2 content in the fuel versus NOx formation (Source: Figure 10 from API 535)[6]



The predictions for NOx emissions in Figure 3.1-1 does not consider the impact of removing olefins from the fuel, which can further reduce the amount of Thermal NOx produced. It is worth noting that Figure 3.1-1 is a typical trend that may not apply to all burners, some new generation burners can mitigate these effects.[6]

RFG is a refinery by-product that is consumed in the refinery to offset the heating demand which would otherwise be required by burning NG or oil given the constituent species cannot be easily recovered as a feedstock, sold as a product or otherwise disposed of.[5] There are significant issues with the disposition of RFG if it is not used as fuel. In many cases RFG would have to be disposed of in a thermal oxidizer or flare if not burned for fuel, which

[5] R. G. Kunz "Environmental Calculations: A Multimedia Approach", Appendix L: Combustion of Refinery Fuel Gas, 2009, John Wiley & Sons, Inc

[6] American Petroleum Institute "Burners for Fired Heaters in General Refinery Services", API RP 535 Third Edition, 2014

does little more than shift the NOx emission to a different location while increasing greenhouse gas emissions. These difficulties outweigh the benefit associated with removal of RFG from the fuel to fired heaters and boilers. Therefore, fuel switching is not expected to be a prominent method to control NOx emissions under proposed Rule 1109.1.

3.1.2 H_2O Injection (Water or Steam)

Techniques that actively cool the combustion zone without extinguishing the flame can reduce peak flame temperature, reducing Thermal NOx formation. Injecting H_2O as either water or steam into the combustion zone is one option that has been used to reduce adiabatic flame temperature. H_2O that is injected into the combustion zone absorbs a portion of the energy that is released when fuel is oxidized and sends this out the stack with flue gas. One drawback with H_2O Injection is the portion of heat that is absorbed from the combustion zone and exhausted to the stack cannot be recovered, which then results in additional fuel consumption and greenhouse gas production.

Thermal NOx formation is influenced by temperature so the injected H_2O needs to be present at the flame front to locally absorb a portion of the heat that is released. The heat that is absorbed by H_2O reduces peak flame temperature thereby reducing the amount of heat that can be absorbed by N_2 and O_2 molecules. If H_2O is not intimately mixed with the fuel at the primary flame front then it's effectiveness for NOx control rapidly decreases.

Water injection is not commonly practiced in the refining industries, due to difficulties in water atomization and injection. Steam, which is a vapor at the point of injection, is more commonly practiced in the industry for use in reducing peak flame temperature and Thermal NOx formation. Feedback from burner vendors shows a 10 to 25% reduction in Thermal NOx formation can be achieved through steam injection depending on the application.

3.1.3 Flue Gas Recirculation (FGR)

FGR is similar in concept to H_2O injection. With FGR a portion of the cooled flue gas is withdrawn from the heat transfer circuit, generally downstream of the convection bank, and is returned back into the combustion zone. In most cases a fan will be required to overcome the pressure drop of the circuit when returning the flue gas. FGR reduces Thermal NOx formation by:[6,7]

(a) Reducing peak flame temperature through the introduction of inert gas (N_2, CO_2, and low concentrations of O_2) into the flame front to absorb a portion of the heat that is released, and

(b) Reducing the partial pressure of O_2 at the flame front by introducing a gas that is depleted in O_2.

FGR is common on forced-draft utility boilers where the returning flue gas temperature is relatively low, FGR return temperatures below 600°F are recommended.[7] Refinery heaters are typically natural-draft and flue gas temperatures in the stack are high, on these units FGR is not performed. FGR with hot flue gas requires insulated ductwork and fans/dampers that operate at high temperature, which reduces reliability. If FGR is to be retrofitted onto an existing unit then additional power to run the fan and plot space to accommodate new equipment is required along with a redesign of the burner to accommodate higher gas rates passing through the throat. Another limitation with FGR exists when there is high pressure drop through the convection section, adding more flue gas into the circuit will exacerbate pressure drop and may limit the amount of draft that can be achieved.

[7] A. Garg "Trimming NOx From Furnaces", Chemical Engineering, November 1992, pp 122 – 128

Recirculation rates are typically limited to 15 to 20% of the total flue gas rate through the heater when firing a gaseous fuel due to flame stability issues, pressure drop constraints across the convection section and a decrease in the net thermal output. Hence, the maximum NOx reduction that can be achieved with FGR for a typical refinery heater is around 50%.[7] FGR does not affect the overall thermal efficiency of the heater when using flue gas downstream of the convection bank. However, FGR does change the duty split between the radiant and convection sections, radiant duty decreases and convection duty increases when performing FGR which may result in a derating of the heater.

3.1.4 Low-NOx Burners (LNB) and Ultra-Low NOx Burners (ULNB)

LNB and newer generation ULNB control the operating conditions at the combustion zone through advanced burner design to achieve low NOx emissions.[8]

3.1.4.1 Staged Combustion

Staged combustion can be segregated into two (2) subcategories:

(a) *Staged-air combustion:* The primary combustion zone adds a small amount of air into the fuel stream (fuel-rich) with the balance of the air progressively added into the flue gas leaving the primary combustion zone.

(b) *Staged-fuel combustion:* The primary combustion zone adds a small amount of fuel into the air stream (ultra-lean) and the balance of the fuel is progressively added into the flue gas leaving the primary combustion zone.

While the specifics around burner design may be quite different between these two subcategories, they both minimize Thermal NOx formation through a combination of lower peak flame temperature and altered reactant concentrations at the flame front. In the primary zone the combustion is either fuel-rich (staged-air) or ultra-lean (staged-fuel) and Thermal NOx formation is low, taking advantage of the two extremes in Thermal NOx formation versus equivalence ratio depicted in Figure 2.1-1. Only a portion of the fuel is burning in the primary zone, which means a greater volume of unburned fuel/air is present to absorb the energy released and quench peak flame temperature. In the secondary and sometimes tertiary combustion zones, the balance of the air (staged-air) or fuel (staged-fuel) is progressively introduced into the combustion products of the primary zone, which allows time for the combustion products to radiate heat to the surrounding cold plane surface and continually cool the flame front as combustion occurs. The air-fuel ratio for the overall combustion process is not altered with staged combustion, just the manner by which the air and fuel come together and combust. Hence thermal efficiency of the unit is unchanged.

3.1.4.2 Internal Flue Gas Recirculation (IFGR)

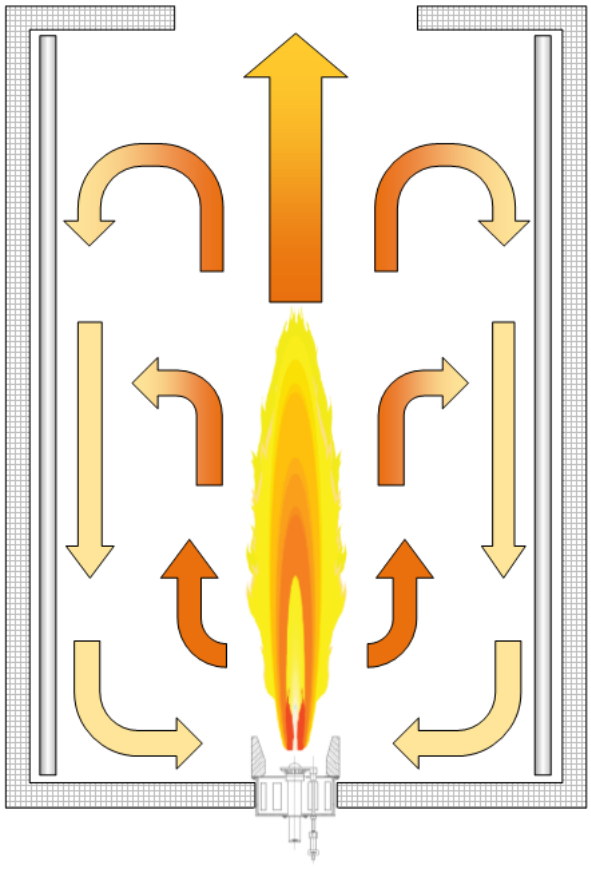
Per discussions in Section 2.1, the flame front is rapidly cooled as the combustion products radiate heat to the surrounding cold plane surface. In addition, flue gas that is closer to the cold plane surface continues radiating heat and further cools. This creates a temperature profile through the radiant section where cool flue gas is located nearer the cold plane surface and warmer flue gas is located around the flame. As flue gas temperature cools the buoyancy of the resulting mixture decreases and an internal circulation pattern arises where cooler flue gas moves

[8] A. Garg "Specify Better Low NOx Burners For Furnaces", Chem. Eng. Progress, January 1994, pp 46 – 49

around the outside of the radiant section to the floor while warmer gas rises near the flame. A region of flue gas is present at the floor that is cooler than the combustion products around the flame front, see Figure 3.1-2.

Through appropriate burner design, cooler flue gas along the floor of the radiant section can be drawn into the combustion zone and used to actively cool the flame, achieving the same end result that external methods like H_2O Injection and FGR use to cool the combustion zone. ULNB use the available pressure of the fuel or combustion air as the motive fluid to draw cool flue gas into the combustion zone.

Figure 3.1-2: IFGR profile that arises in the radiant section of a refinery heater.



3.1.4.3 Burner Technology Status

Typical NOx emissions obtained from an "idealized" burner installation as a function of the technology utilized when burning a gaseous fuel is summarized in Table 3.1-1.

Table 3.1-1: Typical NOx emissions when burning a gaseous fuel (Source: Table 13 API 535)[6]

Technology utilized	Lower NOx level, ppmv Indicative of NG	Upper NOx level, ppmv Indicative of RFG
Traditional burner	60	> 100
Staged combustion	20	60
Staged combustion + IFGR	10	20

Table 3.1-1 shows a significant reduction in NOx emissions can be achieved when changing from a traditional raw gas burner to new generation ULNB. Commercially available and field-proven ULNB like the Callidus® CUBL, John Zink Hamworthy COOLstar®, and Zeeco® GLSF Free-Jet all combine various aspects of staged combustion and IFGR to achieve low NOx emissions.

It is important to note the NOx emission levels shown in Table 3.1-1 were obtained from a test furnace where issues such as burner spacing, burner interaction and heater condition were not a consideration. Retrofitting ULNBs into an existing heater that was designed for raw gas burners can rarely achieve these numbers and the vendor guarantee for long term operation with these burner technologies can be as much as two times the upper NOx level indicated in Table 3.1-1. To achieve minimum NOx emissions using ULNB requires several design criteria to be followed.

(a) *Flame Length:* Traditional raw gas burners rapidly mix the air and fuel air to produce a stable, high intensity flame with a flame length that is in the 0.6 to 1.0 ft/(MMBtu/hr) range. Using techniques that delay combustion (i.e. staged combustion) increases the envelope where combustion is occurring and flame lengths with newer ULNB are greater than 1.25 ft/(MMBtu/hr). This translates into a flame that is almost 50% longer than the flame length from a traditional raw gas burner. A radiant section that is firing with ULNB needs to be long enough to avoid flame impingement on internal surfaces.

(b) *Heat flux / heat density:* High firing rates in a small radiant section produces high floor heat flux (measured as BTU/h firing rate per square foot of floor area) and/or high volumetric heat density (measured as BTU/h firing rate per cubic foot of radiant section volume). When these values are high (typical industry values for "high" are floor heat flux > 300,000 BTU/h/ft^2 and volumetric heat density > 30,000 BTU/h/ft^3) a plug flow pattern arises in the radiant section with very little cool IFGR available to actively cool the combustion zone. This results in higher average flame temperatures and increased NOx emissions when using ULNB. These high thresholds are not a limitation for traditional raw gas burners and limit the effectiveness of ULNB's in retrofit applications.

(c) *Fuel Conditioning:* ULNB designs utilize high velocity fuel gas jets to induce flue gas recirculation and to delay fuel combustion. To create the high velocity gas streams the designs must employ small fuel port sizes that tend to plug/foul if the source of the fuel is not clean. Plugged/fouled tips can result in unstable firing and higher NOx emissions. API 535 recommends the use of filters and/or coalescers to remove aerosols, scale, condensables and other particulate material that could plug ULNB fuel ports. Traditional raw gas burners have larger ports that are less prone to plugging/fouling.

(d) *Burner Spacing:* Compared to conventional raw gas burners, ULNB require greater distances between burners to take advantage of IFGR patterns and the volume over which staged combustion is occurring. If appropriate spacing is not available adjacent burners start interacting, which impacts the combustion profile from the burner and flame stability. In the extreme case, flame interaction between burners can result in a coalescing flame which increases flame length and the potential for flame impingement. A coalescing flame will also increase NOx emissions. In addition to burner-burner spacing, the spacing between burners and heater internals must be appropriate to avoid flame impingement.

(e) *Turndown:* Some ULNB have demonstrated flame stability issues at low firebox temperatures. In order to prevent burner instability and potential flameouts, these burners must often be operated at elevated excess O_2 during turndown operation. Operation at high excess O_2 results in increased NOx emissions, decreased combustion efficiency and higher greenhouse gas emissions.

For a new heater, ULNB are the standard and the heater can be designed accordingly to meet all of these objectives for safe, stable operation at both design and turndown while maintaining low NOx emissions. For older heaters designed with prior burner technologies the above mentioned criteria are rarely achieved when upgrading to newer ULNB. In situations where an existing heater is constrained, as mentioned earlier, upgrading to ULNB may not achieve the lowest NOx emission level demonstrated by the technology.

We have seen guarantees for LNB/ULNB provided by burner vendors like John Zink, Callidus and Zeeco to be in the 20 to 50 ppmv NOx range for typical refinery fuel gas (RFG) streams depending on the application. When these burners are provided as a retrofit option and the burner spacing is sub-optimal, we have seen the NOx guarantees typically fall in the 32 to 38 ppmv range. On occasion, retrofits with ULNBs have been unable to achieve less than 50 ppmv. For a heater that has enough room to optimally space the burners, or for a new heater that can optimize burner spacing, we have seen NOx guarantees closer to the 20 ppmv range.[9]

Burner vendors continue to make progress on designs to further reduce NOx emission levels. While they are all reporting success in the laboratory and in test furnaces at sub 10 ppmv NOx emission levels on NG and in some cases a simulated blend of RFG, there are very few commercial demonstrations to date.

(f) *ClearSign Core™:* A key design feature of the ClearSign technology is the inclusion of custom engineered ceramic elements located downstream of the fuel/air/IFGR mixing point in the combustion zone.[10] Air enters the combustion zone along with high pressure fuel (20 to 35 psig range), which draws in cool flue gas via IFGR, to create a thoroughly mixed oxygen deficient combustible gas that enters an open combustion zone populated with ceramic elements of varying orientation with a net similarity in function to a radiant burner. Staged combustion is not performed in the ClearSign technology. The key advantage of the combustion zone ceramic elements is its superior gray-body radiative heat transfer properties, allowing the ceramic elements to radiate heat from the flame front far more rapidly and effectively than gray-gas radiative heat transfer in the flame front can provide. Combustion is complete in general proximity to the radiating ceramic elements, maintaining very short flame lengths. ClearSign claim low NOx emissions can still be achieved even when floor heat flux density exceeds 300,000 BTU/h/ft^2 due to the radiative heat transfer characteristics of the ceramic elements. A recent advancement was the inclusion of a pilot into the burner envelope which eliminated the need for a separate start-up burner. Installing a pilot burner also overcame a major obstacle with the acceptance of this burner for general refinery use. Several other improvements have been made to

[9] NEC discussions with SCAQMD on 10/11/2019 (project note 19-9009-007)
[10] R. Ruiz & D. Kendrick "New Technology Slashes NOx Emissions at California Refinery", Oil & Gas Journal, March 2017, pp 56 – 62

increase turndown capability, reduce start-up time and improve the ease by which maintenance is performed.[11] The ClearSign Core burner can operate with H_2 content as high as 75 vol% in the fuel.

The first installation of a ClearSign burner was in 2016 at the Tricor Asphalt plant in Bakersfield, CA. In 2019 ClearSign upgraded this burner, a single 8 MMBtu/hr burner using the first generation Duplex design, to a single 15 MMBtu/hr ClearSign Core burner to allow for increased firing rates. In early 2020, ClearSign started a 40 MMBtu/hr demonstration unit at World Oil in Los Angeles, CA using the previous generation Plug & Play design (5 x 8 MMBtu/hr burners). However, testing revealed interaction between the burners which created problematic flame behavior. The decision was made to remove the burners from service and return the old burners into service until the anomaly could be addressed.[12] In June 2020, ClearSign announced a contract with ExxonMobil to supply their latest Core burner technology into several multiburner process heaters at ExxonMobil's Baytown Texas facility.[13] ClearSign are actively selling and marketing the Core burner technology as capable of achieving 8 to 9 ppmv NOx emissions with very low CO emissions. At present, the ClearSign Core burner can only be floor and wall mounted, no roof mounted design presently exists.

(g) *John Zink Hamworthy SOLEX™:* The John Zink Hamworthy SOLEX burner takes advantage of staged combustion and IFGR through a combination of air/fuel premixing in the AIRmix zone and remote fuel staging in the COOLmix zone to achieve low NOx emissions. With this design, reported NOx emissions are in the 5 ppmv range and CO emissions are near-zero while achieving flame lengths that are shorter than 1 ft/(MMBtu/hr).[14] The SOLEX burner is capable of being wall, floor or roof mounted and can operate with high H_2 content in the fuel. During a recent public working group meeting for the SCAQMD, a representative from John Zink confirmed the SOLEX™ technology requires a forced and an induced draft fan along with an advanced burner control scheme to achieve low NOx emissions.[15] For existing natural draft heaters this makes retrofit options challenging. At present there are no commercial demonstrations of the SOLEX burner in operation.

3.1.4.4 Duct Burners

Another category of burners used in a refinery setting is the duct burner, with applications including flue gas reheat at the inlet to an SCR and supplemental fuel firing in reciprocating engine/combustion turbine exhaust for additional steam generation in a downstream HRSG/steam generator.

Thermal NOx formation is low in duct burners due to the following operating conditions:

(a) O_2 content in the flue gas is lower than ambient air so the concentration of one of the reactants has been reduced,

(b) Duct burners are spread out over a large area inside the duct allowing a large volume of flue gas to be mixed into the flame front, taking up some of the heat of combustion to reduce peak flame temperature,

(c) Duct burners operate at low adiabatic flame temperature, typically less than 1,600°F where the reaction kinetics for NOx formation are slow.

[11] NEC discussions with ClearSign on 8/6/2019 (project note 19-9009-001)
[12] https://clearsign.com/clearsign-technologies-corporation-provides-updates-on-ongoing-projects/
[13] R. Brelsford "ExxonMobil lets Contract for NOx-Reducing Technology at Baytown Refining Complex", Oil & Gas Journal, June 2020, Announcement
[14] NEC discussions with John Zink Hamworthy on 9/10/2019 (project note 19-9009-003)
[15] SCAQMD Working Group Meeting #9, December 12, 2019

For these reasons duct burners are sometimes referred to as a "low NOx burner".[16] If the O_2 content in flue gas decreases too far then supplemental ambient air will be required to maintain sufficient O_2 at the flame front. If ambient air is required then flame temperature in a duct burner closely resembles a traditional burner and NOx emissions will increase.

Some of the challenges and issues observed with duct burner designs include imbalanced and/or long flames, inadequate flow/O_2 distribution across the burner, antiquated instrumentation/controls and metallurgical considerations versus localized operating temperatures. Depending on the age of an existing technology, replacing an old duct burner with a modern duct burner design can achieve anywhere from 10 to 25% reduction in NOx emissions.[17]

3.1.5 Flameless Combustion

Flameless combustion is not a new concept, with patent filings in the early 1990s describing the inherent benefits of flameless combustion and low NOx emissions in combustion chambers.[18] The philosophy behind flameless combustion is an extreme example of staged combustion, the combustion zone is now spread out over a large majority of the radiant section to create near-homogeneity in the temperature distribution. Traditional heater designs like that shown in Figure 3.1-2 have dedicated areas in the radiant section where a flame envelope exists, generally characterized by a CO isosurface in the 1000 to 2000 ppmv range based on CFD modeling.[19] Temperatures within the flame envelope of a traditional heater approach the adiabatic flame temperature. In flameless mode, the fuel and air are mixed and burn in a large volume of flue gas so now staged combustion is occurring with excess diluent (flue gas) that absorbs a large portion of the heat of combustion. In flameless mode the temperature variation across the radiant section is typically within 300 to 400°F from the hottest flame temperature to the coolest pocket of flue gas. In a traditional heater with a dedicated flame envelope this same variation can be as high as 2000°F.[20] As a result, the temperature in a flameless radiant section operates in the 1500 to 1900°F range throughout and NOx emissions are routinely in the sub 10 ppmv range.

3.1.5.1 Flameless Combustion Technology Status

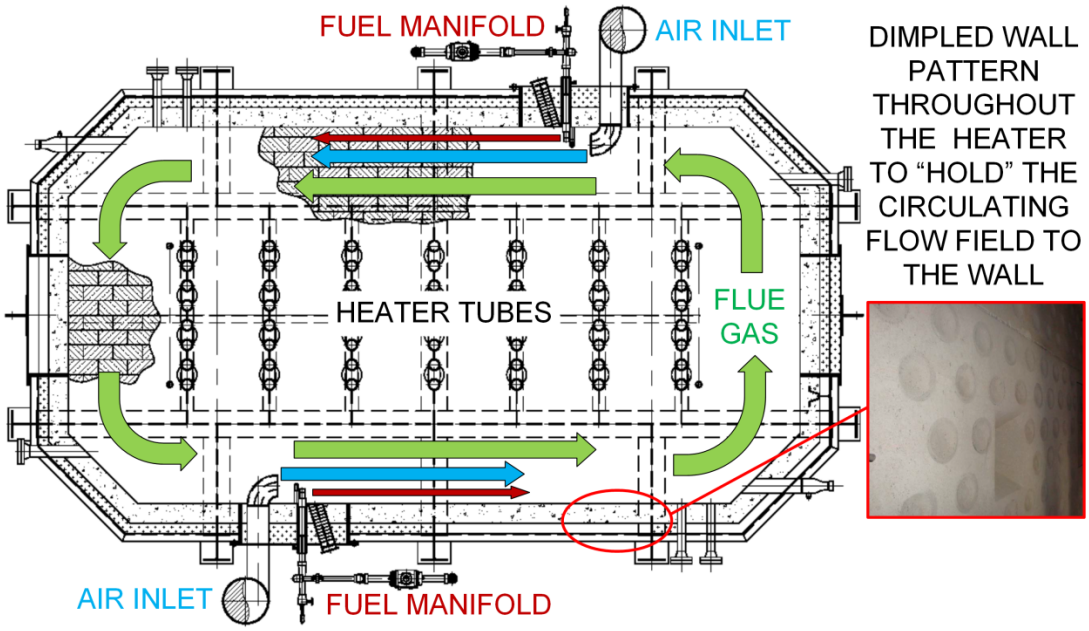
While US patents for flameless combustion were appearing in the early 2000s,[20, 21] radiant sections that employ flameless combustion were not embraced across the refining industry. The general concern with flameless combustion is the ability to detect and verify that combustion is still occurring. In a traditional heater the flame is anchored at a discrete position on the burner tile that typically includes a pilot assembly to ensure combustion is occurring, this also allows flame rods/flame scanners to be inserted that can provide feedback confirmation of combustion to maintain safe and stable operation. With flameless combustion a pilot burner is optional and industrially accepted detection methods like flame rods/flame scanners are not sensitive enough to identify the dispersed nature of the combustion zone. Flameless combustion requires advanced control methods to ensure combustion is still occurring. In general flameless combustion relies on the principle that the entire radiant section

[16] C. E. Baukal Jr (editor) "The John Zink Hamworthy Combustion Handbook", Second Edition, Volume 3 – Applications, Chapter 4: Duct Burners, 2013, Taylor & Francis Group, LLC
[17] NEC discussions with Alstam on 4/30/2020 (project note 19-9009-015)
[18] J. Wünning "Method and Device for Combustion of Fuel in a Combustion Chamber", EU Patent 0463218, Granted 11/23/1994
[19] C. E. Baukal Jr (editor) "The John Zink Hamworthy Combustion Handbook", Second Edition, Volume 1 – Fundamentals, Chapter 13: CFD-Based Combustion Modeling, 2013, Taylor & Francis Group, LLC
[20] W. C. Gibson, R. L. Gibson & J. T. Eischen "Method To Facilitate Flameless Combustion Absent Catalyst Or High Temperature Oxident", US Patent 6,796,789, Granted 9/28/2004
[21] S. L. Wellington, T. Mikus, H. J. Vinegar, J. M. Karanikas "Method for Ignition of Flameless Combustion", US Patent 6,269,882, Granted 8/7/2001

is above auto-ignition temperature and that fuel and air, provided they come together in appropriate proportions, will burn in the flue gas. Part of the advanced control system involves a startup sequence that can get a cold radiant section up above the auto-ignition temperature at which point the hand-off to flameless combustion occurs. The ability to switch back and forth between burner-assisted heating mode and flameless combustion mode to ensure safe and stable operation that is tolerant to the swings in heat load and firing rate of a refinery heater presents a challenge for this technology. Despite these challenges, the development of a flameless combustion system for refinery applications has made some progress in recent years.

(a) *Great Southern Flameless (GSF):* In April 2013 the CVR refinery in Coffeyville, KS started a 9.5 MMBtu/hr crude heater that runs in parallel with the main crude heater using GSF technology, see Figure 3.1-3.[22] This heater has operated for 6 years and maintains around 5 ppmv NOx emissions firing on RFG. The air and fuel enter the heater tangentially and combust along the wall in a circulating flow field before eventually separating and migrating out through the convection opening. An air preheater is required along with a forced draft and induced draft fan to preheat the air and move flue gas around the radiating chamber. A diverter valve in front of the convection section diverts hot flue gas to the air preheater to maintain combustion air temperature at or above 850°F during turndown operation.

Figure 3.1-3: Great Southern Flameless Heater



Flameless combustion provides near-uniform heat flux to the tubes and Great Southern have found both the longitudinal and circumferential maldistribution factors approach 1.0 with this design. There is the possibility for a 52% reduction in radiant coil surface area when compared to conventional heater design which apply a combined longitudinal and circumferential maldistribution factor > 1. Increased radiant section efficiency

[22] http://www.greatsoutherngroup.com/papers/A&WMA-2014-The-Worlds-First-Flameless-Crude-Heater-Rev.pdf

can also lead to reduced surface area requirements in the convection section, almost 90% of the total heat duty can be achieved in the radiant section of the heater with the GSF design. Great Southern have confirmed that the GSF heater has not been pigged to clean the inside of the coil in 6.5 years. This is further confirmation of the uniform heat flux that can be achieved in flameless combustion mode.[23] The GSF radiant section looks quite different to a traditional heater radiant section and the complexity with retrofitting this technology onto an existing heater will be complicated and in many cases may simply not be possible. Figure 3.1-3 shows the tubes are arranged in the center of the radiant section and combustion occurs around the walls, this is not how most heater coils and combustion zones are configured in a traditional refinery heater.

[23] NEC discussions with Great Southern on 9/18/2019 (project note 19-9009-005)

3.2 End of Pipe Solutions

There are three technologies available that make use of a reducing/oxidizing agent to remove NOx from a flue gas stream downstream of a combustion zone. The difference between these technologies is a function of the reagent used, either reducing with ammonia NH_3 and urea $CO(NH_2)_2$ or oxidizing with Ozone O_3, the operating temperature, and the requirement for a catalyst.

3.2.1 Selective Non-Catalytic Reduction (SNCR)

When NH_3 is injected into a flue gas stream that contains NOx at elevated temperature, the following reactions occur.

$$4\ NH_3 + 4\ NO + O_2 \xrightarrow{high\ temperature} 4\ N_2 + 6\ H_2O$$

$$4\ NH_3 + 2\ NO_2 + O_2 \xrightarrow{high\ temperature} 3\ N_2 + 6\ H_2O$$

$$4\ NH_3 + 5\ O_2 \xrightarrow{high\ temperature} 4\ NO + 6\ H_2O$$

SNCR is represented by the first two reactions, which occur in the absence of a catalyst, while the third reaction is the conversion of NH_3 to Fuel NOx which should be avoided. When urea $CO(NH_2)_2$ is used, it thermally decomposes to produce NH_3 and HNCO (isocyanic acid) with NH_3 becoming the SNCR reagent and HNCO combusted. The conversion of NOx to N_2 via SNCR is maximized under the following operating conditions:

(a) *Temperature:* The temperature window for SNCR is in the 1650 to 1900°F range, higher temperatures will produce Fuel NOx from NH_3 while the kinetics are too slow at lower temperatures to achieve meaningful conversions.[1] In some cases an additional reagent such as H_2 can be added into the SNCR reagent to perform Enhanced SNCR (ESNCR) which can decrease the temperature window below 1650°F.[24] However, ESNCR does not improve the level of NOx reduction that can be achieved, it merely opens up the effective temperature window for SNCR.

(b) *NSR (NH_3-to-NOx Stoichiometric Ratio):* NO typically makes up 95+% of the NOx in flue gas so the stoichiometric value is around 1.05 for the SNCR reaction set. Increasing the amount of NH_3 relative to NOx in the flue gas increases the extent of SNCR conversion as NOx becomes the limiting reagent. Typical NSR values for SNCR range between 0.5 and 3.[24] Increasing NSR also increases NH_3 slip and stack emissions will now contain a regulated pollutant that must be controlled. Therefore, NSR is generally limited based on the stack emission threshold for NH_3.

(c) *CO concentration:* SNCR must be performed downstream of the combustion zone where CO has fully burned out of the flue gas, research shows CO suppresses SNCR by competing for the hydroxyl free radicals that are required for NO to be converted to N_2.[24]

(d) *Residence time / mixing:* Residence time in the half a second range is required at the optimal temperature to react NOx via SNCR. As temperature decreases the reaction kinetics slow down and the required residence time increases.

(e) *Mixing:* The reagent needs to be well dispersed in the flue gas for SNCR to be effective. Without adequate mixing NH_3 is only treating a portion of the flue gas stream and sub-optimal NOx reduction will be achieved

[24] J. L. Sorrels "Cost Reports and Guidance for Air Pollution Regulations", Section 4 NOx Controls, Chapter 1 Selective Non-Catalytic Reduction, April 2019, https://www.epa.gov/economic-and-cost-analysis-air-pollution-regulations/cost-reports-and-guidance-air-pollution

even if the residence time and temperature are appropriate. Mixing of the reagent into the flue gas is achieved through dedicated injectors located around the wall of the adiabatic chamber and parameters like the spray angle, injection velocity and orientation of the spray are all critical to SNCR performance. Due to the high operating temperature, injectors are typically located in the walls of the combustion devices injecting reagent across the flue gas flow path, reliability is a concern with an array of injectors located inside the adiabatic chamber.

3.2.1.1 SNCR Technology Status

The challenge with SNCR is to achieve the necessary level of reagent mixing into the flue gas downstream of the combustion zone and to then hold this mixture at the optimal temperature for the required period of time to allow the SNCR reaction to proceed.

A major limitation is most refinery units do not have an appropriate adiabatic chamber available to perform SNCR, the combustion zone is typically inside a radiant section where cold plane surface area is present that rapidly cools the products of combustion below the SNCR temperature window. Issues associated with making the necessary geometry available at the optimal temperature window prohibits SNCR from all but a few select heaters in the refinery. Therefore, SNCR is generally limited to units where an adiabatic chamber is present downstream of the combustion zone.[25]

SNCR is more effective when the inlet NOx concentration is high. NOx reduction is seen to decrease as the inlet concentration of NOx decreases and SNCR is generally recommended when the inlet NOx concentration is above 100 ppmv.[26] Therefore, SNCR has limited effectiveness when combined with a NOx control technology like ULNB where NOx concentration will be in the 20 to 40 ppmv range entering the SNCR region.

The upper limit on NOx reduction that can be achieved for a unit that is designed and optimized for SNCR operation is ~70%. However, when retrofitting an existing unit practical limitations on the geometry, the ability to mix the SNCR reagent and constraints with NH_3 slip mean NOx reduction levels of 20 to 40% are typically observed in the field.

Considerations when selecting the reagent to use, either urea or ammonia, are site specific based on several factors including reagent cost, concentration, safely transporting, storing and handling the reagent and the equipment required to get the reagent into a suitable state for injection into the flue gas.

3.2.1.2 Concerns with Ammonium Bisulfate (ABS) Formation

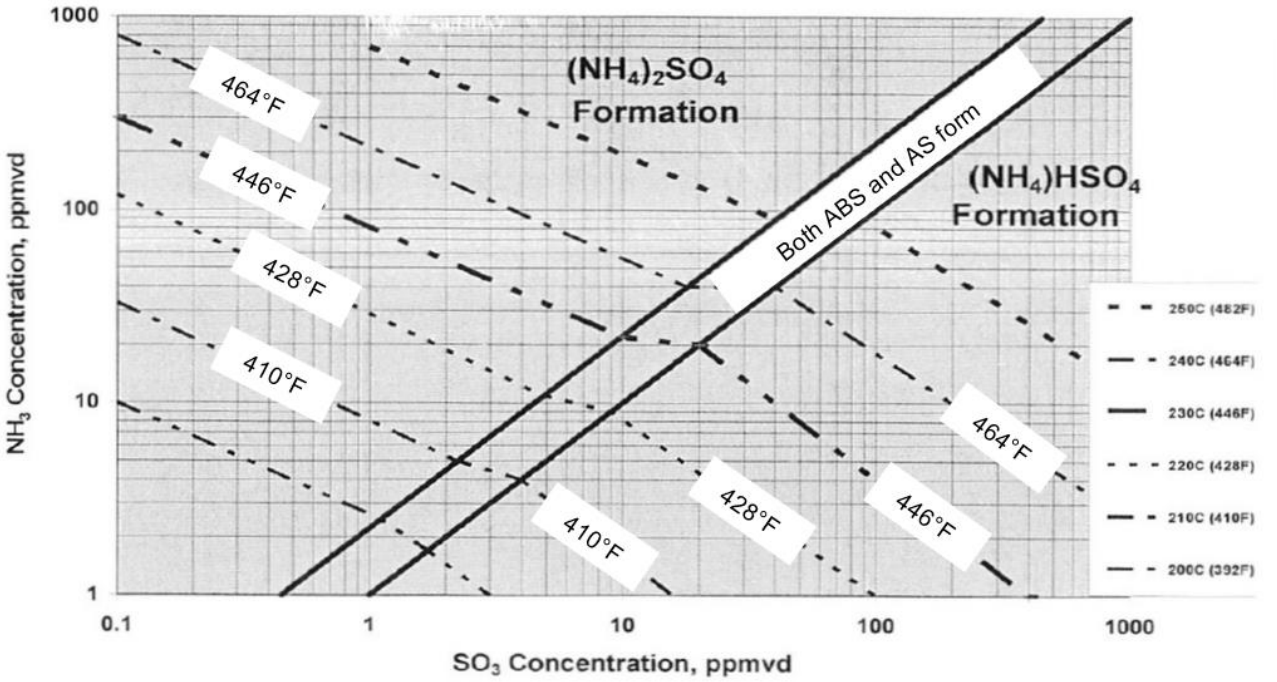
The combustion products from sulfur species in the fuel are primarily SO_2 and a small amount of SO_3. Excess NH_3 that does not react with NOx via SNCR can react with SO_3 and moisture on cooler surfaces in the flue gas circuit to form ammonium salts, namely ABS $(NH_4)HSO_4$ and/or ammonium sulfate $(NH_4)_2SO_4$. ABS is a sticky solid which can deposit and form a coating that is difficult to remove on heat transfer surfaces in the convection bank or air preheat equipment. This coating can reduce heat transfer performance and will promote under-deposit corrosion of metal surfaces (tubes). The type and the amount of ammonium salts that form will depend on the molar ratio of SO_3 to NH_3 in the flue gas. The Hitachi-Zosen chart is used to make this determination, see Figure 3.2-1. RFG and NG contain low amounts of sulfur and ABS is typically not a concern when burning these fuels.

[25] Institute of Clean Air Companies (ICAC) "Selective Non-Catalytic Reduction (SNCR) for Controlling NOx Emissions", White Paper. Prepared by the SNCR Committee of ICAC, February 2008

[26] American Petroleum Institute "Post Combustion NOx Control for Fired Equipment in General Refinery Service", API RP 536 Second Edition, 2006

However, in some cases the flue gas will contain higher levels of SO_3 (i.e. flue gas from an FCCU regenerator or Claus Plant) and methods to avoid and/or accommodate ABS formation should be factored into the design of these systems.

Figure 3.2-1: Hitachi-Zosen chart for ABS and Ammonium sulfate formation (Source: Figure 7 API 536)[26]



3.2.2 Selective Catalytic Reduction (SCR)

Similar to SNCR, SCR involves the use of a reducing agent, either urea or ammonia, to convert NOx to N_2.

$$4\ NH_3 + 4\ NO + O_2 \xrightarrow{temperature + catalyst} 4\ N_2 + 6\ H_2O$$

$$4\ NH_3 + 2\ NO_2 + O_2 \xrightarrow{temperature + catalyst} 3\ N_2 + 6\ H_2O$$

The main difference for SCR as compared to SNCR is that the temperature is lower and NH_3 conversion to Fuel NOx is essentially eliminated. However, a suitable catalyst is required to increase the reaction rate and maximize the NOx reduction that can be achieved at low temperatures. One advantage with SCR catalyst when using urea as the reagent is the hydrolysis of HNCO can be accommodated on the catalytic surface to generate an additional NH_3 molecule.

Catalyst design has advanced over the years and modern SCR catalysts use a range of active ingredients such as platinum, vanadium, zeolite, TiO_2, ZrO_2, WO_3 and V_2O_5 that are structurally supported on a stable, high surface area substrate to facilitate the reaction.[27]

Factors that impact the conversion of NOx to N_2 via SCR are summarized below:

(a) *Temperature:* The temperature window for SCR can range between 400 to 1100°F depending on the formulation of the catalyst, low temperature applications generally utilize rare earth elements in the catalyst, medium temperatures between 500 and 800°F typically utilize metal oxides in the catalyst and high temperature applications commonly utilize zeolite in the catalyst.

(b) *NSR (NH_3-to-NOx Stoichiometric Ratio):* As with SNCR, the stoichiometric ratio required to remove one mole of NOx from the flue gas is around 1.05. In general a NSR ratio of 1.05 will result in an asymptotic NOx reduction level of about 85% and NSRs above stoichiometric are required to improve the NOx reduction achieved. NSR ratios typically do not exceed 1.2 to balance high NOx reduction against NH_3 slip.

(c) *Superficial velocity:* Superficial velocity, measured as flue gas volumetric rate divided by the front-face area of the catalyst, is an important design parameter that sets the size of the catalyst bed and ultimately the plot area required for the SCR system. Lower superficial velocity equals a greater NOx reduction but this also means a bigger catalyst inventory is required, increasing cost and plot space. Upper values for superficial velocity are set by the vendor to balance reaction kinetics against NOx reduction while practical limits such as cost, plot space and flue gas distribution over the front-face area of the catalyst limits at the low end. A recommended target for ultra-low NOx emissions is 10 ft/s or lower at the inlet to the SCR.

(d) *Mixing:* Even distribution of NH_3 and NOx is required over the entire front-face area of the catalyst bed to maximize NOx reduction and minimize NH_3 slip. Another important consideration is the even distribution of flue gas flow across the front-face area of the catalyst bed. Mal-distribution of NH_3 and/or flue gas will result in sections of the catalyst bed operating at high superficial velocity and/or low NSR, which impacts the overall NOx reduction that can be achieved. In general, the SCR vendor will design the Ammonia Injection Grid (AIG), any required flue gas distribution enhancements (such as straightening vanes), and the SCR catalyst to ensure the reagent is well mixed in the flue gas prior to entering the SCR catalyst. Typical SCR flue gas operating temperature allows the AIG to be located inside the ductwork upstream of the SCR catalyst bed as an array of nozzles along with bluff bodies to promote mixing. Computational Fluid Dynamics (CFD) is

[27] J. L. Sorrels "Cost Reports and Guidance for Air Pollution Regulations", Section 4 NOx Controls, Chapter 2 Selective Catalytic Reduction, June 2019, https://www.epa.gov/economic-and-cost-analysis-air-pollution-regulations/cost-reports-and-guidance-air-pollution

performed to verify AIG design. Uniform NH_3 distribution and flue gas flow entering the SCR catalyst bed are both critical to achieving low ppmv NOx emission levels.

(e) *Pressure drop:* The addition of a catalyst layer in the flue gas circuit adds pressure drop that must be factored into the design and operation of upstream combustion sources and systems.

(f) *Catalyst selectivity:* When SO_2 is present in the flue gas some active catalyst ingredients, most notably vanadium, are known to promote an unwanted side reaction $SO_2 + ½ O_2 \rightarrow SO_3$. SO_3 is a regulated pollutant species that must be controlled and flue gas streams containing a measureable quantity of SO_2 need to account for this reaction with the selection of an appropriate catalyst formulation. The presence of SO_3 can also result in ABS formation on downstream heat transfer surfaces, see Section 3.2.1.2. Another concern with ABS formation is the potential for fouling due to capillary condensation inside the pores of the SCR catalyst. According to the Kelvin equation, ABS formation inside nanometer-sized pores of the catalyst structure occurs at much higher temperatures than the Hitachi-Zosen chart of Figure 3.2-1 for bulk phase condensation.[28] ABS formation in the catalyst micropores can be somewhat mitigated by increasing the temperature of the catalyst to evaporate ABS, but the means to do this needs to be incorporated into the design.

In other cases the SCR catalyst can include additional components such as palladium to provide dual functionality for CO/VOC removal without impacting NOx reduction performance.

(g) *Catalyst activity:* During normal operation SCR catalyst will slowly deactivate and the reaction rate, which is a function of catalyst activity, decreases over time. Factors that contribute to deactivation include catalyst aging, thermal sintering, plugging/fouling of the catalyst support structure, plugging/fouling at the pore-mouth of the microporous channel leading to the active catalyst sites, mechanical erosion and catalyst poisoning. Designing an SCR system for continuous run lengths of several years means the catalyst must achieve the guaranteed NOx reduction level with end-of-run activity while maintaining NH_3 slip at the regulated value. Therefore, SCR systems are designed so that catalyst end-of-run operation can maintain the guaranteed performance and can accommodate turnaround schedules

When designing a new unit to include SCR all the factors described above can be accommodated in the design for optimal SCR performance. When retrofitting SCR to an existing unit there are several important considerations that arise in addition to the general points raised above.

(i) A new SCR catalyst bed will increase pressure drop in the existing flue gas circuit. The air flow through a natural-draft heater is limited and the addition of an induced draft fan (new power consumer) will be required to maintain throughput. For balanced draft systems the existing fans may need to be upgraded (i.e. new impeller or replace existing fans, bigger motors, increased power consumption) to maintain throughput.

(ii) For an existing system the heat transfer coil needs to be assessed to determine where the appropriate location will be to withdraw flue gas, process it through the SCR catalyst bed and then reinsert this back into the heat transfer coil. In some cases large sections of the heat transfer coil may need to be replaced. Available plot space may further impact the required duct runs to get to/from the SCR catalyst bed. The added pressure drop for new duct runs on top of a new SCR catalyst bed may add even more backpressure on the system that needs to be addressed in point (i) above.

[28] C. J. Bertole "Method for Enhanced Low Load SCR Operation", Power Plant Pollutant Control and Carbon Management "MEGA" Symposium, August 2016

(iii) Expert review is often required to assess the mechanical integrity of the upstream heater and ductwork when operating pressure increases. Equipment on the flue gas side of a heater typically have low allowable working pressures.

(iv) If complications arise trying to insert the SCR system into the existing heat transfer coil then an alternative is to perform SCR at the end of the flue gas circuit before it is released to the atmosphere. Flue gas can be diverted from the stack to a duct burner to reheat the gas before entering the SCR catalyst. The duct burner will increase flue gas temperature back up to the optimal window for SCR but will also increase greenhouse gas emissions and unit energy consumption. After SCR the treated flue gas is returned to the stack for release. In this scenario low temperature SCR catalyst will be preferred to minimize the reheat duty required.

(v) If ammonia or urea are not currently used in the refinery then an appropriate reagent needs to be selected. This decision will be site-specific and is based on several factors including reagent cost, concentration, safely transporting, storing and handling the reagent and the equipment required to get the reagent into a suitable state for injection into the flue gas.

(vi) Existing units are generally space constrained and locating the SCR and ancillary equipment (i.e. ammonia/urea tanks, pumps, vaporizer, piping, etc.) within the available on-site plot space or remotely is an important operational consideration.

3.2.2.1 SCR Technology Status

Catalyst activity and SCR reliability are two critical factors for refinery operators to avoid an unplanned shutdown due to SCR mal-operation. Despite these concerns, SCR systems have demonstrated long and reliable run life in the field on many flue gas applications and can be considered a mature technology with a high degree of industry acceptance. Historically, SCR units in refinery applications have demonstrated high reliability at NOx emission levels above 10 ppmv, limited information is available for SCR reliability at sub 10 ppmv NOx emissions levels.

A cross-section of the SCR market and capabilities of the technology from discussions with vendors who actively participate in the refining sector shows: [29,30,31]

(i) SCR designs can achieve 92 to 94% NOx reduction in a single catalyst bed with NH_3 slip in the 5 to 10 ppmv range. A system that is designed to achieve 90+% NOx reduction will typically be a custom engineered installation that is verified through CFD analysis to minimize channeling/bypassing and to ensure good mixing is achieved upstream of the SCR catalyst bed.

(ii) Multiple catalyst beds, often times with an additional AIG between the beds, is required to achieved NOx reduction levels greater than ~94%. The addition of catalyst beds is the most effective means of ensuring that SCR systems can reliably achieve sub 10 ppmv NOx emission levels. Multiple catalyst beds can be accommodated in a single structure. Vertical height typically increases while plot space is largely unchanged for a multi-bed installation.

(iii) A trade-off is required between low NH_3 slip and high NOx reduction. Most vendors will avoid installing an NH_3 destruction bed downstream of their SCR catalyst bed and prefer the system operate at low NH_3 slip through engineering design. If required, an NH_3 destruction bed can be installed.

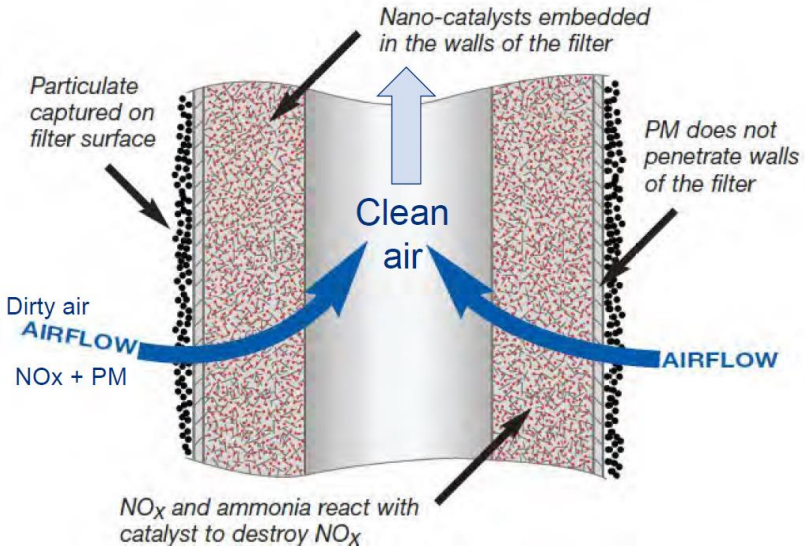
[29] NEC discussions with Shell Catalyst & Technology on 8/8/2019 (project note 19-9009-002)
[30] NEC discussions with CECO Peerless on 10/24/2019 (project note 19-9009-008)
[31] NEC discussions with Umicore on 1/9/2020 (project note 19-9009-012)

(iv) Some catalyst technologies allow the SCR to operate at lower temperatures with some systems achieving 90+% NOx reduction in the 300 to 400°F range.[29] These low temperature systems can achieve comparable performance to higher temperature systems by installing additional catalyst beds.

(v) Design of the catalyst, the catalyst support and method of attachment in the structure are important considerations to ensure long term performance of the SCR, especially when targeting sub 10 ppmv emission levels. Examples of known issues with SCR installations in the refining industry include erosion from catalyst fines in the flue gas from an FCCU regenerator, ceramic fibers from lined equipment blocking flow area, catalyst poisoning due to chromium volatilization out of the alloy tubes in a Steam Methane Reformer (SMR), ABS fouling in the catalyst pores if SO_3 is present at low operating temperature, and mechanical failures of the sealing mechanism between catalyst modules that would normally prevent flue gas bypassing.

SCR installations that are designed to handle PM in the flue gas (i.e. SCR units downstream of a FCCU regenerator) make use of large openings in the support matrix of the catalyst bed to minimize plugging. In addition, soot blowers and top-down flow arrangements are used to keep the support matrix free of blockages. One recent development that combines PM removal with SCR is UltraCat, provided by Tri-Mer, see Figure 3.2-2. Early field demonstrations of this technology from a glass manufacturing furnace shows 85% NOx removal can be achieved from a flue gas stream that contains PM.[32] Additional data from pilot scale testing shows NOx removal can approach the mid-90% range. This is one alternative to traditional SCR for applications where high PM loads are present in the flue gas. UltraCat also has the capability to remove additional contaminants such as SO_2 from a flue gas stream in addition to NOx and PM. In most cases extra equipment is required in the design of the unit to handle other contaminants (i.e. dry sorbent injection system for SO_2 removal; air blowers to remove accumulated PM from the outer surface and hoppers to collect the PM). The plot space required for an UltraCat unit can be as much as 10 to 15 times that required for an SCR.

Figure 3.2-2: Combined PM capture and NOx removal offer in the UltraCat technology from Tri-Mer.



[32] https://epd.georgia.gov/air/sites/epd.georgia.gov.air/files/related_files/document/110811trimerintro.pdf

3.2.3 Low Temperature Oxidation

Injecting ozone into the flue gas at low temperature converts NO to NO_2 and then NO_2 into nitrogen pentoxide, N_2O_5, via the following reactions.

$$O_3 + NO \xrightarrow{gas\ phase\ reaction} NO_2 + O_2$$

$$O_3 + 2\ NO_2 \xrightarrow{gas\ phase\ reaction} N_2O_5 + O_2$$

N_2O_5 is soluble in water and can be removed from the flue gas via wet scrubbing to produce nitric acid, HNO_3.

$$H_2O + N_2O_5 \xrightarrow{vapor/liquid\ phase\ contact} 2\ HNO_3$$

HNO_3 can then be neutralized to form nitrate salts by injecting a base solution into the water, the nitrate salts are then purged from the system for disposal. The preferred operating temperature range is below 300°F due to the half-life of ozone in the system. At temperatures above 300°F the ozone will decay to O_2 before having sufficient contact time with NOx to form N_2O_5. Temperatures below 70°F are not preferred as the reaction kinetics for N_2O_5 formation are slow and the required residence time increases. Side reactions are very slow compared to NOx reaction kinetics (orders of magnitude slower) and good selectivity for O_3 to NOx can be achieved.

Typical residence time for O_3 contact with NOx is a few seconds to achieve high NOx removal rates. NH_3 is not required, alleviating concerns with NH_3 slip in the stack.

3.2.3.1 Low Temperature Oxidation Technology Status

Low Temperature Oxidation (LoTOx™) technology was originally developed by BOC (now owned by Linde) and is provided under an exclusive license agreement through Belco (Clean Technologies division of Dupont) for refinery applications.

Ozone, O_3, is a compound that is rarely used in the refinery and on-site generation is required. The ozone generator passes a stream of high purity oxygen through a series of tubes where a coronal discharge is produced between the dielectric plate and tube wall. A 480 V electrical supply is typically required for the ozone generator along with transformers and rectifiers. The preferred source of oxygen is liquid O_2, reduced efficiency for the production of O_3 is observed when the source of oxygen contains argon and nitrogen impurities from a Vacuum Swing Adsorption (VSA) unit. Typical ozone generators produce a stream that contains ~10 wt% O_3 at pressures in the 20 to 25 psig range. The stoichiometric O_3 requirement is ~1.5 mole O_3 per mole of NOx. Lower NOx emission levels can be achieved with higher O_3/NOx ratios.[33]

The LoTOx system is typically a vertical tower that includes a quench step, if required to reach the preferred temperature window, along with O_3 injectors at the inlet. The LoTOx tower is appropriately sized to achieve the required residence time for NOx conversion to N_2O_5 and subsequent absorption of the N_2O_5 into a basic aqueous solution of sodium sulfite.

LoTOx is not prone to plugging/fouling like SCR systems and has minimal impact on the pressure profile of the existing flue gas circuit. Provided plot space is available, a LoTOx system is equivalent whether this is a new installation or will be retrofitted onto an existing unit. For flue gas streams where SOx and PM emissions control is required, a LoTOx system is incorporated into the Wet Gas Scrubber (WGS) design. Most WGS can be easily

[33] NEC discussions with Belco on 9/19/2019 (project note 19-9009-006)

adapted to handle N_2O_5/HNO_3 removal from the flue gas stream and Belco currently offers LoTOx in tandem with their reverse jet and EDV scrubber systems.[33]

LoTOx can achieve 95+% NOx reduction in a single tower installation. While several LoTOx installations have been deployed on utility boilers and in the glass and steel industries, LoTOx has found limited applications in the refining sector. The cost and plot space required to install a new WGS system, if one does not presently exist, makes LoTOx a less favorable option than other retrofit NOx control technologies. Another complicating factor with LoTOx is the need for O_3 generation. Refineries typically do not have excess capacity for liquid O_2 available and O_3 is a compound that is rarely used with existing refinery technologies. To date, two (2) LoTOx installations are in operation treating flue gas streams downstream of an FCCU regenerator where an existing WGS is available. These units, operating on two separate FCC units owned by Marathon Petroleum, have shown NOx emissions below 10 ppmv can be achieved.[34]

Belco have considered retrofit options where O_3 is injected into an existing WGS to perform LoTOx, which can bypass the need for a new LoTOx tower thereby reducing cost and plot space. However, residence time is limited and NOx removal efficiencies are expected to be low (i.e. 50% or less) as compared to a dedicated LoTOx tower.[33] Options to modify an existing WGS to increase the available residence time are available but are not expected to improve the 50% NOx reduction number by a significant amount. Currently there is no commercial installation that has performed a retrofit to inject O_3 into an existing WGS to perform LoTOx.

[34] Response from N. Larsen, AFPM Q&A and Technology Forum, FCC Q&A Session, New Orleans LA, October 5, 2015

3.3 Assessment of the Existing NOx Control Technologies

Based on technical information provided by vendors and information from technology users, the following assessment can be made for a range of NOx control technologies available under proposed Rule 1109.1.

Table 3.3-1: Assessment of NOx control technologies for proposed Rule 1109.1

Technology	New install applying BACT	Retrofit where the conditions are…			Comments
		Most favorable for the installation	Typical for the installation	Unfavorable for the installation	
Fuel switching to NG	% NOx reduction = 100 x {1 – 1 / [1 + 0.625 x (mol/mol H_2 before switch)] }				Approximation Independent of technology
FGR with staged fuel burner (1)	30 ppmv	> 30 ppmv	< 40 ppmv	< 50 ppmv	Typically applied to boilers
ULNB (1)	15 ppmv	< 20 ppmv	< 35 ppmv	< 50 ppmv	Commercially available ULNBs
Next generation ULNB (1)	> 5 ppmv		< 10 ppmv		Commercial demonstration underway with Clearsign
Flameless combustion (1)	5 ppmv	–	–	–	One demonstration unit on a small heater
SNCR with 5 ppmv NH_3 slip	70% NOx reduction maximum	High inlet NOx (>100 ppmv): 40 to 50% NOx reduction			Limited application due to geometrical considerations
		Low inlet NOx (50 to 100 ppmv): 20 to 40% NOx reduction			
SCR	2 ppmv	2 ppmv			Multiple catalyst beds required
Lo-TOx	10 ppmv	10 ppmv	≤ 90% NOx Reduction	< 50% NOx reduction	Wet Gas Scrubber (WGS) required downstream

(1) Fuel assumed to be RFG unless noted otherwise

4. Individual Refinery Categories Under Proposed Rule 1109.1

In 2014, NEC reviewed the feasibility of SCAQMDs NOx RECLAIM BARCT for five (5) refinery categories:[35]

(i) FCCUs (Fluid Catalytic Cracking Units),

(ii) Refinery heaters and boilers with firing rate > 40 MMBtu/hr,

(iii) Gas turbines and duct burners,

(iv) Coke Calciner, and

(v) Sulfur recovery/tail gas treatment units.

The SCAQMD assigned a NOx BARCT limit of 2 ppmv @ 3% O_2 and NEC determined this to be the lowest achievable NOx emission level for current technologies. The 2014 RECLAIM assessment was adopted in 2015 and is referred to as the "2015 RECLAIM BARCT Assessment". Under proposed Rule 1109.1, further segregation of the categories has been made and some outliers have been identified to develop more specific NOx BARCT limits that are in-line with current industry practice and emerging technologies. Commentary on each of these categories is provided in the following sections.

[35] NEC document 14-045-4 "SCAQMD NOx RECLAIM – BARCT Feasibility and Analysis Review", November 26, 2014

4.1 Process Heaters and Boilers

Table 4.1-1: NOx BARCT limits for heaters and boilers under proposed Rule 1109.1 from SCAQMD

Refinery Equipment Category	No. of Units in Category	Proposed BARCT Limit (ppm)	Corrected O_2%	Proposed Averaging Time	2017 NOx Emissions (tpd)	Cost-Effectiveness
Heaters & Boilers						
Process Heaters						
<20 MMBtu/hr	22	40 / 9*	3	2 hour	0.09	$0
20 - 40 MMBtu/hr	45	30 / 9*	3	2 hour	0.41	$5,000
40 - 110 MMBtu/hr	72	5 / 2**	3	8 hour #	1.96	$35,000
>110 MMBtu/hr	46	5 / 2**	3	8 hour #	2.60	$36,000
Boilers						
<40 MMBtu/hr	5	5	3	2 hour	0.01	$0
40 - 110 MMBtu/hr	3	2	3	8 hour #	0.052	$50,000
>110 MMBtu/hr	20	2	3	8 hour #	2.50	$13,000

* Future effective date.

** Heaters >40 MMBtu/hr that have a permit limit of 5 ppm or less within 6 months of rule adoption, can maintain the 5 ppm limit until a future effective date, or when the SCR is replaced, whichever is sooner.

NEC recommends an averaging time of 24 hours, refer to Section 4.1.1.

There is no issue applying the same BARCT limit for gas fired process heaters and gas fired boilers, in both cases the NOx control technology will be equivalent, ULNB or ULNB plus SCR. NEC recommends the short term NOx BARCT limit be set to 40 ppmv for all heaters with a firing rate below 40 MMBtu/hr (i.e. the 30 ppmv limit for 20 to 40 MMBtu/hr should be set to 40 ppmv) per discussions outlined in Section 3.1.4.3. 40 ppmv is an interim step that allows ULNB upgrades to be implemented in an effort to reduce NOx emissions. Heaters with sub-optimal spacing are expected to be in the high-30 ppmv range for NOx emissions when retrofitted with ULNBs across all firing rates < 40 MMBtu/hr. Heaters and boilers with firing rates < 40 MMBtu/hr typically have a small plot area and are often times packed tightly in a process unit and the cost to retrofit SCR will be high. Unless a major upgrade of the unit is performed it will be very difficult to justify the cost effectiveness of a SCR system.

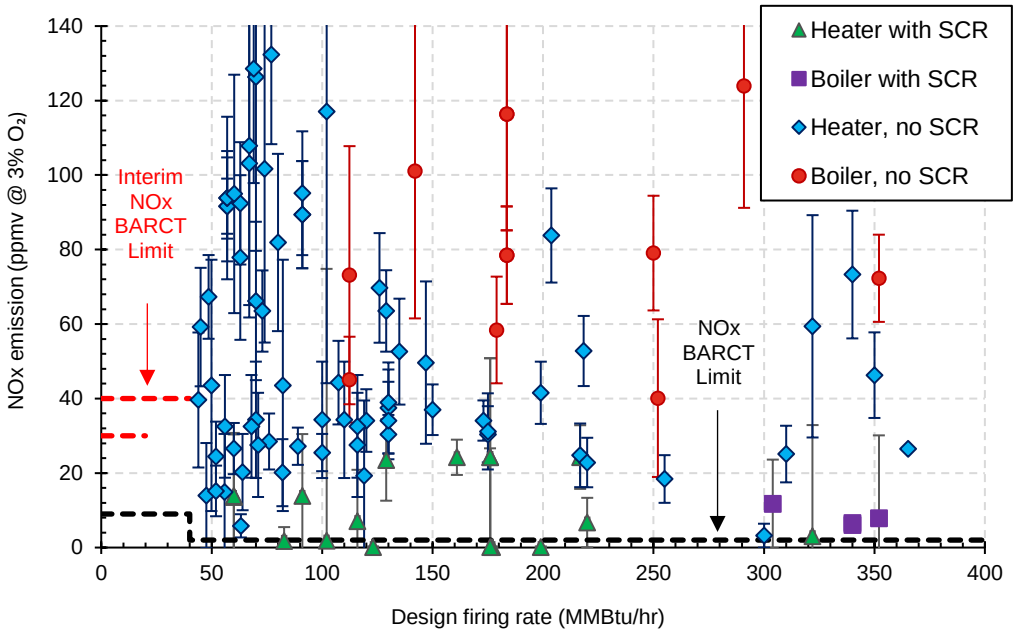
The 9 ppmv NOx BARCT limit for a heater that is replaced after it has reached end-of-life is a long term goal that allows emerging technologies more time to achieve greater market acceptance. Technologies such as the ClearSign Core, John Zink Hamworthy SOLEX and Great Southern Flameless can achieve 5 to 9 ppmv NOx emission as the sole control technology, albeit with a very limited number of reference units in the field. The NOx emission target of 9 ppmv provides some leeway for these emerging technologies if the 5 ppmv value cannot be met.

For heaters and boilers with rated firing rates > 40 MMBtu/hr, a NOx BARCT limit of 2 ppmv will require a combination of ULNB and SCR, there is no emerging burner technology that can achieve NOx emissions this low.

Assuming the concentration of NOx entering the SCR catalyst bed will not exceed 40 ppmv with ULNB installed upstream, a 2 ppmv limit means SCR systems must be able to achieve 95% NOx reduction.

The SCR system will need to operate inside the optimal temperature window to maximize NOx reduction. This represents a narrow region within the existing convection section coil where the flue gas will need to be withdrawn from. If not in the optimum temperature window then over-treatment with NH_3 may be an option. If the SCR system will be located downstream of the existing convection section coil where flue gas temperatures are cooler, or turndown versus design operation means flue gas temperature will drift outside the optimum temperature window, then duct burners may be another requirement.

Figure 4.1-1: NOx emissions from heaters and boilers in the District. Data points represent the average value and bars represent 2 standard deviations. Hourly data over 1 year of representative operation was used.



The 2 ppmv NOx emission limit was considered technically feasible during the NOx RECLAIM BARCT review performed by NEC in 2014.[35] Refinery heaters and boilers in the District that have SCRs are running with NOx levels in the 20 ppmv range or less, see Figure 4.1-1. Ultimately, the decision to set 2 ppmv will have an impact on the number of SCR catalyst beds that need to be installed along with an NH_3 destruction bed if NH_3 slip is a consideration. NEC believes 2 ppmv is technically feasible with designs that include the following features:

(a) Low superficial velocity (< 10 ft/s),

(b) SCR system operating in the optimum temperature window based on the selected catalyst formulation,

(c) Multiple SCR catalyst beds (minimum of two),

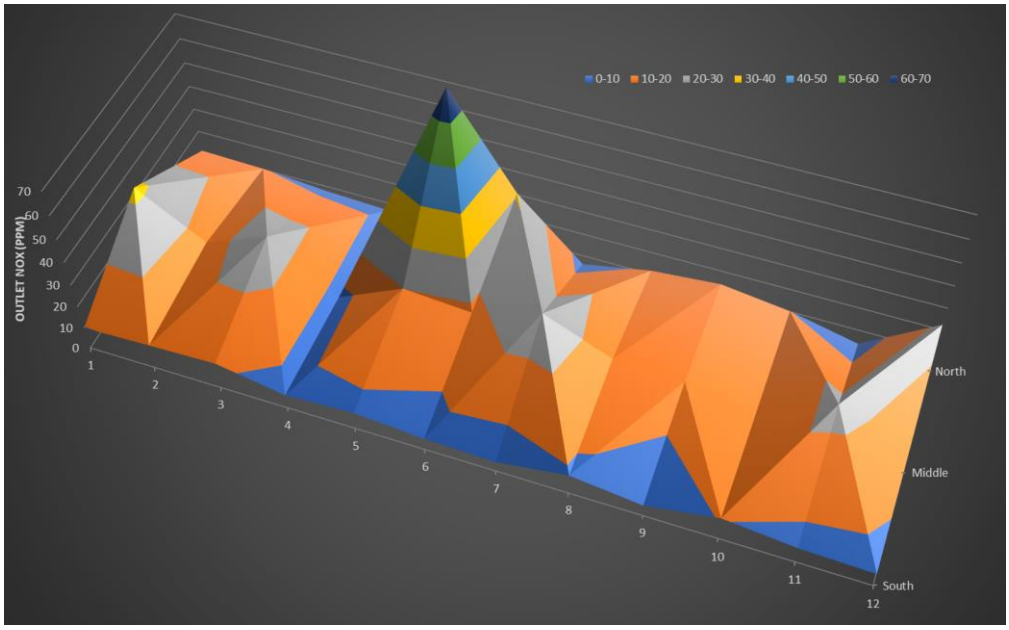
(d) Provision for a secondary AIG for one or more downstream SCR catalyst bed(s),

(e) NH_3 destruction bed, and

(f) Even distribution of ammonia in the flue gas entering the SCR catalyst bed(s).

This will result in additional capital for the SCR system, additional capital cost for a fan (due to increased pressure drop) and additional NH_3/power consumption which should be factored into the cost effectiveness number. The importance of multiple catalyst beds is highlighted in field data obtained from a US refiner that experienced a bypass in one zone of a single bed SCR unit, see Figure 4.1-2. The peak observed in the outlet NOx concentration at zone 5 on the north side leaving the SCR resulted in the average NOx emission level effectively doubling in the stack. To provide tolerance to small deviations like those observed in Figure 4.1-2, which has a significant impact on overall SCR performance, reinforces the need for multiple catalyst beds to maintain low NOx emission levels.

Figure 4.1-2: Contour of NOx emissions measured at various positions leaving a single bed SCR unit that was experiencing bypass in one zone, identified by the large peak at position 5 on the north end.



While SCR vendors prefer improved engineering and design to eliminate the need for an NH_3 destruction bed, it does not eliminate the degradation of performance seen over the course of a run (operating period) which typically requires additional NH_3 to maintain NOx reduction. The combination of both low NOx (2 ppmv) and low NH_3 slip (5 ppmv) will likely necessitate an NH_3 destruction bed for most refinery applications.

4.1.1 Averaging Times

SCAQMD plan to address abnormal periods of operation with SSM provisions in the rule, which will allow for exclusion of data during periods of start-up, shutdown, and equipment malfunction. A malfunction is defined as "any sudden, infrequent, and not reasonably preventable failure of air pollution control, monitoring equipment, or a process to operate in a normal manner, which causes, or has the potential to cause, the emission limitations to be exceeded; the ability to handle short term fluctuations needs to be maintained through an appropriate averaging

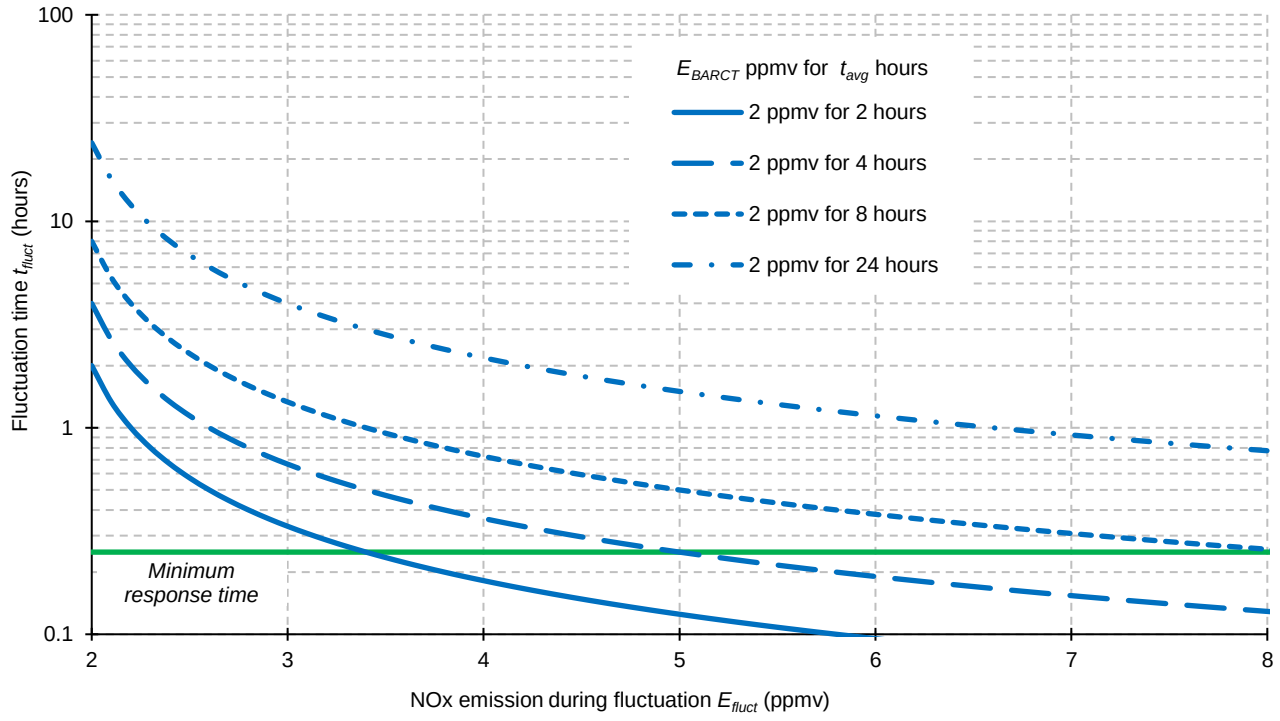
time."[36] Excluding malfunctions, the ability to handle short term fluctuations needs to be maintained through an appropriate averaging time, which impacts equipment complexity and cost with a SCR unit.

To examine the impact of averaging time in more detail, the following simplified equation can be derived.

$$t_{fluct} = E_{BARCT}\, t_{avg}\, DM / [\, E_{fluct} - E_{BARCT}\, (\, 1 - DM\,)\,]$$

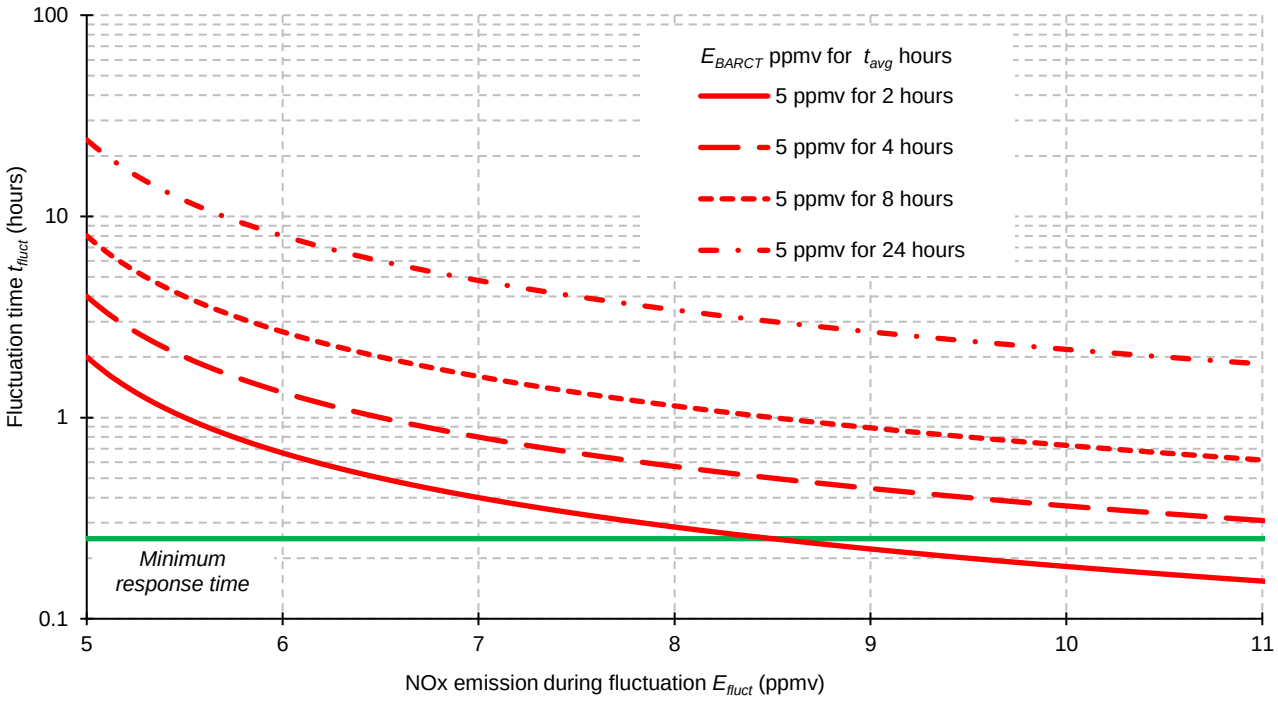
t_{fluct} (hours) represents the allowable period of time that a fluctuation in the NOx emission level occur can occur before exceeding the NOx BARCT limit, E_{BARCT} (ppmv) represents the NOx BARCT limit assigned for the equipment, t_{avg} (hours) represents the assigned averaging time, and E_{fluct} (ppmv) represents the fluctuation in NOx emission level that is occurring. The design margin, *DM* (fractional value), represents a "margin" that is generally applied to the design of equipment to ensure it can meet the guarantee value (i.e. a factor of safety applied to the design). A typical design margin for refinery equipment is 10% so *DM* = 0.1. This means a SCR unit guaranteed for 2 ppmv NOx emission limit will have the capability to run at NOx emission levels in the 1.8 ppmv range. If a fluctuation occurs and the NOx emission level increases to E_{fluct} there is a finite period of time the refinery can take action in order to correct operation and get the equipment back to the 1.8 ppmv range before the NOx BARCT limit is exceeded. Some representative curves for t_{fluct} at various E_{BARCT} and t_{avg} values are presented in Figure 4.1-3 and Figure 4.1-4 by way of example.

Figure 4.1-3: Fluctuation time t_{fluct} for various t_{avg} times with an assigned E_{BARCT} of 2 ppmv under proposed Rule 1109.1 with a 10% design margin. Note the y-axis for fluctuation time is logarithmic.



[36] http://www.aqmd.gov/docs/default-source/rule-book/Proposed-Rules/1109.1/r1109-1-rule-language---11-20-2020-b-cap.pdf?sfvrsn=6

Figure 4.1-4: Fluctuation time t_{fluct} for various t_{avg} times with an assigned E_{BARCT} of 5 ppmv under proposed Rule 1109.1 with a 10% design margin. Note the y-axis for fluctuation time is logarithmic



The green horizontal line in Figure 4.1-3 and Figure 4.1-4 represents a lower limit for response time to take corrective action. This value is consistent with the response time attributed to the corrective action(s) taken by operators in a HazOp (Hazard and Operability study) or PHA (Process Hazards Analysis). If the NOx emission fluctuation E_{fluct} results in a t_{fluct} below the green horizontal line then this is outside the typical response time of the operators and the averaging time is impractical.

With a 10% design margin in the SCR, a NOx BARCT limit of 2 ppmv (blue curves in Figure 4.1-3) and

- averaging time = 2 hours: If the fluctuation exceeds 3.4 ppmv the operators have less than 15 minutes to respond and make corrective action(s). To provide the operators with 1 hour of troubleshooting time means corrective action needs to be taken when the fluctuation exceeds 2.2 ppmv. These results are impractical for a continuously operating unit within a refinery.
- averaging time = 4 hours: If the fluctuation exceeds 5 ppmv the operators have less than 15 minutes to respond and make corrective action(s). To provide the operators with 1 hour of troubleshooting time means corrective action needs to be taken when the fluctuation exceeds 2.6 ppmv. Once again these results are impractical for a continuously operating unit within a refinery.
- averaging time = 8 hours: If the fluctuation exceeds 8.2 ppmv the operators have less than 15 minutes to respond and make corrective action(s). To provide the operators with 1 hour of troubleshooting time means corrective action needs to be taken when the fluctuation exceeds 3.4 ppmv. This is a very tight window for operations to be able to make an informed decision and take action given the guarantee point for the equipment is 2 ppmv.

- averaging time = 24 hours: If the fluctuation exceeds 21 ppmv the operators have less than 15 minutes to respond and make corrective action(s). To provide the operators with 1 hour of troubleshooting time means corrective action needs to be taken when the fluctuation exceeds 6.6 ppmv.

Similar arguments apply when the NOx BARCT limit is 5 ppmv (red curves in Figure 4.1-4), a meaningful fluctuation in the NOx emission level (E_{fluct}) should be detectable before exceeding the minimum fluctuation time to allow corrective action(s) to be taken or to diagnose a malfunction.

Experience has shown that an upset event occurring within a refinery on an infrequent basis that is not part of operations day-to-day routine will require some time to identify and remedy. These abnormal events take several hours to diagnose and if a rapid solution can be deployed then the upset can be rectified within a shift or two (i.e. start standby equipment if the running equipment failed, isolate/clean/return-to-service a plugged sensor, return a valve to it's intended open/close position if it was inadvertently moved, replace a failed piece of equipment with a warehouse spare etc.) An averaging time of 24 hours allows the operators an appropriate window of time to see a meaningful fluctuation in the NOx emission level, diagnose the problem (if it is not a routine day-to-day event) and take the necessary corrective actions(s) before the NOx BARCT emission limit is exceeded. A modest averaging time of 24 hours will minimize unwanted exceedance events and minimize reporting to the authorities if the solution is simple enough to implement within a relatively short period of time. Therefore, NEC recommends the averaging time for SCR units on heaters and boilers with sub 10 ppmv NOx BARCT emission limits be set to 24 hours. This same argument applies to other refining categories that include a CEMS with a proposed averaging time of 8 hours.

Trends presented in Figure 4.1-1 for NOx emission data from a range of heaters and boilers in the District demonstrates the variability observed in running units under normal operation (i.e. equipment is not starting up, shutting down or malfunctioning). The NOx emission data was provided on an hourly basis over 1 year of representative operation. When this data is plotted with the average as a point and 2 standard deviations up/down as the error bar (i.e. covering ~95% of the data assuming a normal distribution), significant spread is observed and these units are not operating at a single point but instead fluctuate throughout a normal operating year. This is also true on units that have an existing SCR. One possible explanation for variability in the observed data with existing SCR units on heaters and boilers is open loop NH_3 injection, which does not actively control fluctuations in the NOx emission level. Implementing control system upgrades to minimize the fluctuations in NOx emission level, along with any redundancy required to reliably automate NH_3 injection into the flue gas, is expected to be a common feature on units with a NOx BARCT limit in the sub 10 pppmv range. Provided the fluctuation in NOx emission level is the result of a normal swing in the operation of upstream equipment then the control system will handle hour-by-hour fluctuations in the NH_3 injection rate. NEC recommends the cost estimates for SCR upgrades factor in the cost required to upgrade the control system for automated feedback control of NH_3 injection based on the instantaneous NOx emission level (if it is not already implemented).

Small heaters and boilers (< 40 MMBtu/hr firing rate), along with thermal oxidizers and incinerators addressed in Section 4.7, do not include a CEMS (Continuous Emissions Monitoring System). The approach with these units is to implement NOx control technology at the source through advanced burner design to reduce NOx emission levels. Provided the burners are operating as designed (i.e. without malfunction) a CEMS can be avoided, reducing costs associated with the upgrade. By removing the need for a CEMS, averaging time now represents source testing duration as performed by an approved third party stack testing company. In this case the averaging time should be set to the typical time for stack testing, which is around 2 to 3 hours. NEC are in agreement with an averaging time of 2 hours for small heaters and boilers (< 40 MMBtu/hr) based on source testing.

4.1.2 Cost Effectiveness

NEC expects the cost and complexity of SCR units in the District to differ from a traditional SCR unit:

- The cost basis for SCR units in the U.S. EPA Cost Spreadsheet is the electric power industry, which does not account for the complexity of executing retrofit projects within an operating refinery. SCAQMD have noted and corrected this discrepancy during a prior working group meeting.[37]
- Most heater/boiler units in the District will require ULNB upgrades in addition to SCR retrofits to achieve sub 10 ppmv NOx BARCT limits. NEC's prior experience with ULNB upgrades in refinery units (which also required upgrades to supply piping and other ancillaries in the fuel gas system) shows the price range is in the $2MM to $3MM range.[9] SCAQMD have included the costs required to upgrade ULNBs into the cost estimate for SCR projects when required.
- With low NOx BARCT limits, NEC expects the SCR system to be two de-NOx catalyst beds with ammonia injection grids (AIG) before each bed, followed by an ammonia destruction bed for a total of three catalyst beds and two AIGs. SCAQMD have noted in several working group meetings that multiple catalyst beds in addition to an ammonia destruction bed needs to be factored into the configuration of SCR units in the District.[37, 38, 39]
- Refineries will want to install automated equipment (if not already installed) to minimize reliance on operator intervention to maintain sub 10 ppmv NOx emission levels on a continuous basis. SCAQMD have noted that recent applications for new SCR projects include facilities to perform automated feedback control that modulates NH_3 injection as part of the SCR design.
- Higher NH_3 treat rates are expected at sub 10 ppmv NOx emission levels so there may be a requirement to increase the size of existing NH_3 handling equipment. SCAQMD have factored new and/or replacement equipment into the cost estimate for cases where an increase in NH_3 injection rate is required.

NEC are in agreement with the approach the SCAQMD has taken to develop cost effectiveness number for each refining category, which addresses the points highlighted above regarding the cost and complexity of these units.

[37] http://www.aqmd.gov/docs/default-source/rule-book/Proposed-Rules/1109.1/pr1109-1-wgm_9_final.pdf?sfvrsn=12
[38] http://www.aqmd.gov/docs/default-source/rule-book/Proposed-Rules/1109.1/pr1109-1-wgm_10_final.pdf?sfvrsn=18
[39] http://www.aqmd.gov/docs/default-source/rule-book/Proposed-Rules/1109.1/pr1109-1-wgm-11-final.pdf?sfvrsn=6

4.2 SMR (Steam Methane Reformer) Heaters

Table 4.2-1: NOx BARCT limits for SMR heaters under proposed Rule 1109.1 from SCAQMD

Refinery Equipment Category	No. of Units in Category	Proposed BARCT Limit (ppm)	Corrected O_2%	Proposed Averaging Time	2017 NOx Emissions (tpd)	Cost-Effectiveness
Heaters & Boilers						
SMR Heaters						
PSA-off Gas/RFG/NG	11	5	3	8 hour #	1.02	$15,000

NEC recommends an averaging time of 24 hours.

There are several salient differences between the heater in a SMR and a traditional heater/boiler that will contribute to higher NOx emissions upstream of the SCR:[40]

(a) The SMR fuel composition is constantly changing making it difficult to operate the SMR at low flue gas O_2 levels, increasing Thermal NOx formation vs traditional heater/boiler burners,

(b) The SMR fuel source rapidly swings in H_2 content which will results in a periodic swing in Thermal NOx formation,

(c) The SMR combustion zone operates at significantly higher flue gas temperatures than a typical refinery heater/boiler which will result in higher Thermal NOx formation.

At the beginning of the PSA blowdown step, the adsorber vessel contains a large amount of CO_2 and smaller amounts of H_2, CO and CH_4 that is sent to the SMR heater through a buffer drum. Once the adsorber vessel has depressurized, a slipstream of H_2 is pushed through the vessel and H_2 content of the tail gas increases. See Figure 4.2-1 for a simulated profile of the gas composition leaving a PSA vessel that was generated from a dynamic process simulator of a H_2 PSA unit. The time scale for Figure 4.2-1 is around 3 to 5 minutes for a typical H_2 PSA unit.

While the buffer drum between the PSA vessel and heater helps to smooth out the peaks and troughs in Figure 4.2-1, it does not remove the underlying swing and the SMR heater is subjected to this cyclic profile during normal operation.

This variation in fuel composition over the course of several minutes makes heater tuning very difficult and the SMR heater usually runs at higher excess O_2 (above the optimum value) to control the O_2 trough that corresponds with the H_2 peak in PSA tail gas (i.e. keep O_2 in the flue gas above a minimum safe operating limit).

Another complicating factor is the SMR heater runs at very high average temperature, typically greater than 2,100°F to drive the endothermic reaction in the tubes. These high temperatures are a result of:

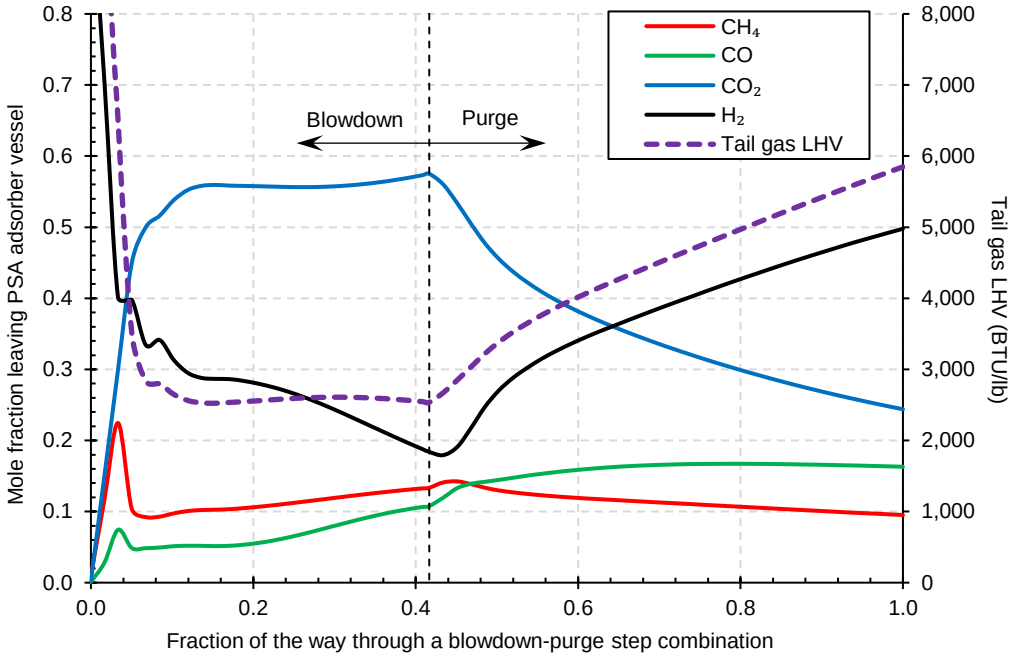
(i) High average radiant section temperature (in the range where thermal Thermal NOx formation is significant)

[40] NEC discussions with SCAQMD on 1/7/2020 (project note 19-9009-014)

(ii) High H_2 content in the fuel (high adiabatic flame temperature)

These factors makes it difficult to find a suitable burner that does not result in high NOx formation. Another complicating factor is SMR heater design is unique to each licensor and the resulting heat flux profile down the length of the tube is an important criteria when selecting an appropriate burner.

Figure 4.2-1: Composition profile leaving a PSA adsorber vessel during the purge and blowdowns steps of a H_2 PSA cycle during normal operation

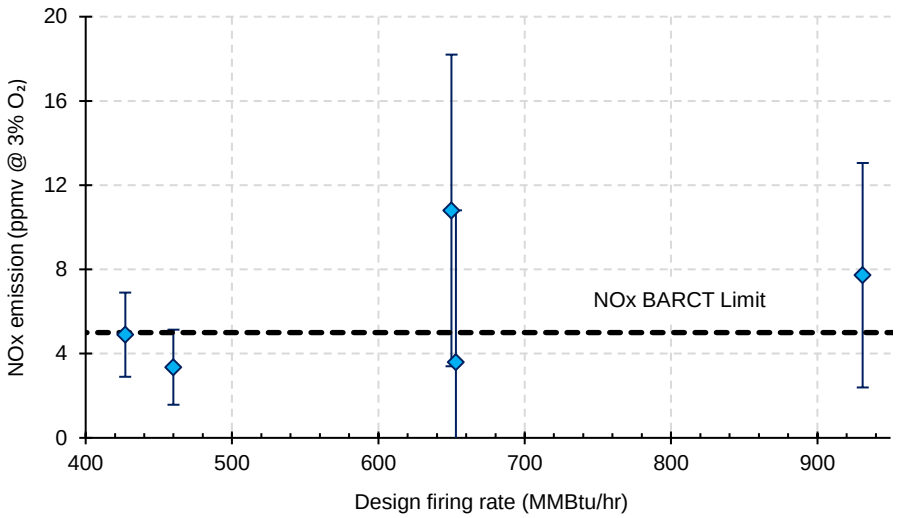


LNB/ULNB's rely on staged combustion and IFGR to reduce high temperature combustion zones in the radiant section and thereby reduce thermal NOx formation. SMR heater burners are designed to delay flue gas combustion to provide a very uniform flue gas temperature profile in the radiant section. However, the SMR heater is a high intensity heater operating with high flue gas temperatures and limited heat transfer surfaces so it does not provide cool flue gas to the burner flame eliminating one of the core NOx reduction features of LNB/ULNBs, flame cooling via IFGR.

The variability of SMR fuel composition impacts not only the average Thermal NOx formation in the SMR heater but also the variability of the flue gas NOx composition with time (PSA cycle). To achieve low final outlet NOx emissions with low NH_3 slip, on a continuous basis, NH_3 addition to the flue gas upstream of the SCR would have to be modulated on a "feed forward basis". Considering the response time of analytical instruments (NOx measurement), the short residence time of flue gas passing from the SMR through the waste heat recovery section to the SCR's AIG, the response time for NH_3 rate changes and the continuously changing purge gas composition, will make it difficult to control instantaneous NOx emissions in the sub-5 ppmv range.

The addition of a second catalyst bed to the SCR will achieve lower NOx emissions. However, as noted above, the cyclically varying fuel composition makes it difficult for both NOx and NH_3 control to the same levels achieved in a heater/boiler configuration at a similar firing rate.

Figure 4.2-2: NOx emissions from SMRs in the District. Data points represent the average value and bars represent 2 standard deviations. Hourly data over 1 year of representative operation was used.



The District currently has 11 SMR heaters, 6 of these run with PSA off gas while 5 of these run on RFG (the PSA off gas does not go directly back into the SMR heater). Short term oscillations in fuel composition are mitigated in the 5 units running on RFG but the furnace still operates at high temperature and the fuel contains H_2. Therefore, NOx emissions would be comparable whether the SMR heater is running with PSA off gas or RFG, the main difference will be short term oscillations are mitigated in the 5 units running on RFG. Although SMR heaters present complications when assessing options to reduce NOx formation, SCR units have proven effective at controlling NOx emissions from these units and NEC will note a NOx BARCT limit of 5 ppmv is the lowest practical value that could be applied to this category.

The existing SMR heaters in the District are meeting, or are close to meeting, a NOx BARCT limit of 5 ppmv, see Figure 4.2-2. Most of these units already have SCR installed so a small incremental reduction in NOx emissions will be required. SCAQMD estimates that 25% of the TIC for a new SCR would be required to upgrade an existing unit to achieve the proposed NOx BARCT limit. NEC estimates a new SCR unit would be in the $30 to $40 MM range. Based on this preliminary estimate the cost for upgrades is in the $7.5 to $10 MM range. The estimated cost for these upgrades is higher than SCAQMD's estimate, which is in the $4 MM to $7.1 MM range. Annual O&M operating costs will be expected to increase as a result of increased NH_3 consumption and increased power demand. The addition of a second catalyst bed into the SCR will increase pressure drop through flue gas the circuit, which correspondingly increases the power consumption of the ID fan.

Based on similar arguments presented in Section 4.1.1, NEC recommends the averaging time be extended to 24 hours.

4.2.1 Unique Case: Integrated SMR Heater and GTG (Gas Turbine Generator)

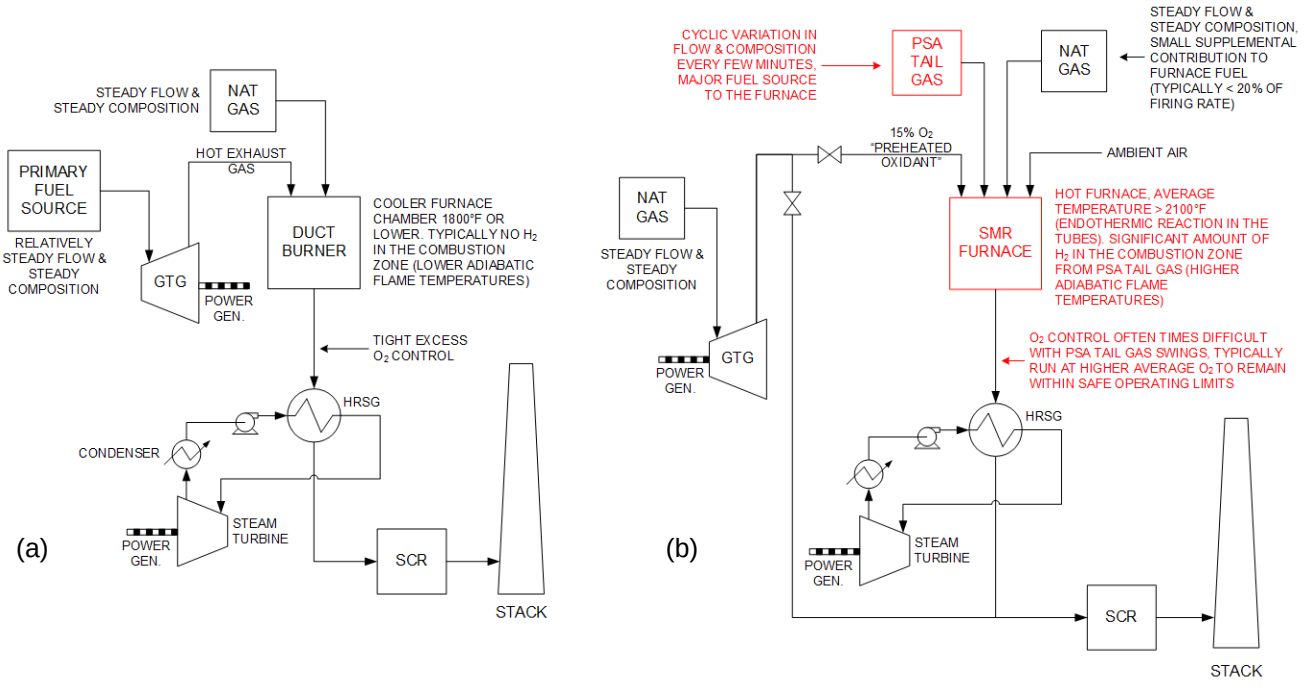
Table 4.2-2: NOx BARCT limits for integrated SMR and GTG under proposed Rule 1109.1 from SCAQMD

Refinery Equipment Category	No. of Units in Category	Proposed BARCT Limit (ppm)	Corrected O_2%	Proposed Averaging Time	2017 NOx Emissions (tpd)	Cost-Effectiveness
Heaters & Boilers						
GTG & SMR Heater						
PSA/NG/RFG	2	5	15	8 hour #	0.082	$0

NEC recommends an averaging time of 24 hours.

One location in the District uses flue gas from a GTG as the source of oxidant to a SMR heater. This unique installation looks similar on paper to a combined cycle co-generation, see Figure 4.2-3.

Figure 4.2-3: (a) Traditional combined cycle co-generation unit versus (b) Integrated GTG and SMR unit that is installed in the District



With a combined cycle co-generation unit, the fuel source to the duct burners can be NG or a blend of NG and RFG. The auxiliary fuel gas supply composition in the combined cycle co-generation unit will be more consistent than the fuel supply to the SMR, which varies continuously based on the discussion in Section 4.2. Although the

SMR/GTG combination may look similar on paper to a combined cycle co-generation unit, there are several salient differences between these systems which will contribute to higher NOx emissions upstream of the SCR:

(a) The SMR fuel composition is constantly changing making it difficult if not impossible to operate the SMR at low flue gas oxygen levels increasing Thermal NOx formation versus a duct burner configuration,

(b) The SMR fuel has high H_2 content in the fuel which will result in higher Thermal NOx formation,

(c) The SMR combustion zone operates at significantly higher flue gas temperatures than a typical duct burner which will result in higher Thermal NOx formation.

From this perspective it will be difficult to apply the NOx emission level for GTG or combined cycle cogeneration units to this particular instance due to the presence of the SMR heater. NEC notes that 5 ppmv has been applied as the NOx BARCT limit, which is in-line with the earlier discussion around SMR heaters.

Based on similar arguments presented in Section 4.1.1, NEC recommends the averaging time be extended to 24 hours.

4.3 Sulfuric Acid Plant Heaters

Table 4.3-1: NOx BARCT limits for sulfuric acid plant heaters under proposed Rule 1109.1 from SCAQMD

Refinery Equipment Category	No. of Units in Category	Proposed BARCT Limit (ppm)	Corrected O_2%	Proposed Averaging Time	2017 NOx Emissions (tpd)	Cost-Effectiveness
Heaters & Boilers						
Sulfuric Acid Plant						
Furnace	2	30	3	365 day	0.097	$50,000
SU Heaters/boilers	3	Low Use				

Just like SMR heaters, the fuel that is burned in a Sulfuric Acid Plant heater is different from traditional heaters and boilers and was broken out into its own category. The fuel burned in a Sulfuric Acid Plant heater typically contains elevated levels of sulfur-bearing species. Facilities in the District have stated that 60% or more of the feed to the Sulfuric Acid Plant heater is spent acid. Feed to the Eco-Services Sulfuric Acid Plant heater consists of spent acid (60%) and molten sulfur (40%) with NG the combustion fuel. The Sulfuric Acid Plant at the Phillips 66 Wilmington facility is primarily spent acid with H_2S as the combustion fuel (RFG is used to maintain flame only). These heaters run at very high combustion zone temperatures, > 2,000°F and the heater itself is an adiabatic chamber that does not contain cold plane surface area to actively cool the flue gas. With high combustion zone temperature and no cold plane surface area in the adiabatic chamber common techniques like staged combustion and IFGR are very difficult to implement and commercially available ULNBs will have very little impact on Thermal NOx formation. The adiabatic chamber is too hot for SNCR to provide any realistic NOx reduction.

The application of post-combustion NOx control technologies is difficult as the flue gas contains elevated levels of SO_2 and SO_3. The concern with NH_3 and SO_3 being present together in the flue gas over SCR catalyst is the potential to form ABS, which results in fouling through capillary condensation in the catalyst pores. For SCR to be effective in this application the SO_3 must be removed first, which requires the flue gas to be quenched below H_2SO_4 saturation temperature. This quench step produces a fine mist of corrosive sulfuric acid. Removing sulfuric acid mist requires a wet scrubber unit before the H_2SO_4-free gas can then be reheated to SCR reaction temperature. Another potential option is LoTOx. Both of these post-combustion options were found to be expensive and therefore, not cost effective at a NOx BARCT limit of 5 ppmv.

The division of John Zink that handles sulfuric acid plants and thermal oxidizers stated they have custom designed burner technologies that can specifically handle the harsh environment and high levels of sulfur, which requires a more robust burner design. In one example John Zink demonstrated a 70% reduction in NOx emissions from a facility in Texas through the use of their custom designed burners. Eco-Services currently use a John-Zink staged-air low NOx burner on their Sulfuric Acid Plant heater which is producing NOx emissions around 25 ppmv. Eco-Services stated these burners were custom-designed for their heater at a cost of $5 MM. The Phillips 66 Wilmington Sulfuric Acid Plant heater is producing NOx emissions of ~28 ppmv and currently has on NOx mitigation technology in place.

NOx emissions from the two Sulfuric Acid Furnaces in the District are below 30 ppmv. The only cost effective solution that has been found to date is to implement a robust burner design that is custom-engineered to the heater for a cost of ~$5 MM. With this implementation NOx emissions are expected to be in the 25 ppmv range based on the example at Eco-Services in the District. The Sulfuric Acid Plant heater at Phillips 66 Wilmington is producing around 28 ppmv and is unlikely to see a significant reduction in NOx emissions with the implementation of the advanced burner design upgrade from John Zink.

NEC is in agreement with the 30 ppmv NOx BARCT limit for Sulfuric Acid Plant heaters. 365 days is an appropriate averaging time based on the operating variability of these units.

4.4 FCCU (Fluid Catalytic Cracking Unit)

Table 4.4-1: NOx BARCT limits for FCCU under proposed Rule 1109.1 from SCAQMD

Refinery Equipment Category	No. of Units in Category	Proposed BARCT Limit (ppm)	Corrected O_2%	Proposed Averaging Time	2017 NOx Emissions (tpd)	Cost-Effectiveness
Other Categories						
FCCU						
Regenerator & CO Boiler	5	2 5	0	365 day 7 day	0.83	$32,000
SU Heaters(1 heater ULSD)		Low Use				

The common sources of NOx from an FCCU are:

(a) NOx formed in the regenerator, and

(b) NOx formed in the combustion zone of a CO Boiler downstream of the regenerator in a partial burn FCCU configuration.

FCCU regenerators operate at temperatures where Thermal NOx formation is very low. Therefore, the primary source of NOx originates from nitrogen-bound species in the coke on catalyst, akin to Fuel NOx.

Use of CO promoter additives to control CO emissions and afterburning in FCCU regenerators has also historically resulted in increased NOx emissions, especially those promoters that utilize platinum. Non platinum additives have been developed by most FCC catalyst suppliers that can help in providing CO promotion without the generation of additional NOx.

Some FCC catalyst suppliers offer an additive that can reduce NOx formation in full burn mode operation. These additives, such as Grace DENOX[41] and Johnson Matthey NOXGETTER,[42] catalytically convert NOx and NOx precursors to N_2. NOx reductions in the 40 to 50% range are typically quoted with these additives, which alone will not achieve the NOx BARCT limit required for FCCUs in the District.

Another option is to remove the source of nitrogen from the feed to the FCCU. ConocoPhillips (now Phillips 66) presented data from an FCCU running in full burn mode that was processing "super hydrotreated" feed (very low sulfur and nitrogen levels).[43] While NOx and SOx emissions from the FCCU regenerator were very low, CO emissions were high, in the 1,000 to 4,000 ppmv range. The only reliable way to control CO emissions was to

[41] https://grace.com/catalysts-and-fuels/en-us/fcc-additives/NOx-Reduction
[42] M. Genç, A Gül, E. B. Dalgıç, Ş. Avcılar & T. Ventham "Taking steps to reduce FCC NOx emissions", Hydrocarbon Engineering, July 2018
[43] W. Henning "NOx and CO Emission Interactions in FCCU 9", presented at the NPRA Cat Cracker Seminar, Houston TX, August 19 – 20, 2008

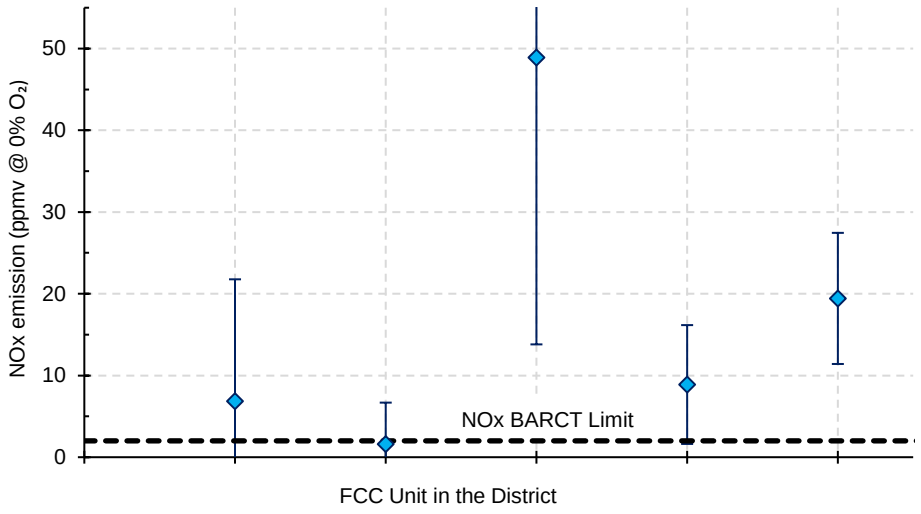
increase flue gas NOx content (i.e. adding sour feed to the FCCU, injecting quinoline into the FCCU feed, injecting NH_3 or NOx into the regenerator air).

Running highly hydrotreated FCCU feed to reduce NOx emissions is likely to increase CO emissions from the FCCU regenerator. Therefore, the only practical solution to reduce NOx emissions is to implement an end-of-pipe solution. The combustion zone of the CO Boiler can introduce an additional source of NOx into the flue gas from the FCCU regenerator through Thermal NOx formation as discussed for heaters and boilers, as well as through combustion of precursor species from the FCCU regenerator. The CO Boiler is typically a combustor and a heat recovery coil for generating superheated steam. In some instances the combustor is an adiabatic chamber that may allow SNCR to be performed, however the NOx reduction with SNCR will not be sufficient to meet the NOx BARCT limit.

The baseline NOx emission level from the FCCU regenerator, combined with an additional NOx load from the CO Boiler, is most effectively treated downstream of the CO Boiler. The common method used in existing FCCUs is SCR. In some cases a WGS is located downstream of the CO Boiler to remove SOx and PM from the flue gas prior to release to the atmosphere. In these cases where a WGS is already installed, LoTOx is another option.

SCR systems have been specifically designed to handle the highly erosive and sulfur-containing flue gas stream from an FCCU regenerator/CO Boiler and is expected to continue being the technology of choice in the District.

Figure 4.4-1: NOx emissions from existing FCCUs in the District. Data points represent the average value and bars represent 2 standard deviations. Hourly data over 1 year of representative operation was used.



The majority of the FCCUs in the District are operating in the 1.5 to 17 ppmv range for NOx emissions, see Figure 4.4-1. SCR systems are already installed on most of these FCCUs and the ability to reach the NOx BARCT limit of 2 ppmv will require retrofit features such as lower space velocity (larger unit footprint, essentially an entire replacement), additional catalyst beds, increased NSR, more AIGs and/or NH_3 destruction bed to be considered.

365 days is an appropriate averaging time based on the operating variability of these units.

4.5 Gas Turbines (Firing on NG and/or RFG)

Table 4.5-1: NOx BARCT limits for gas turbines under proposed Rule 1109.1 from SCAQMD

Refinery Equipment Category	No. of Units in Category	Proposed BARCT Limit (ppm)	Corrected O_2%	Proposed Averaging Time	2017 NOx Emissions (tpd)	Cost-Effectiveness
Other Categories						
Gas Turbines with Duct Burners						
NG/RFG/Mixed Gas	8	2	15	8 hour #	0.98	$27,000
Gas Turbine without Duct Burners						
NG/RFG	2	2	15	8 hour #	0.34	

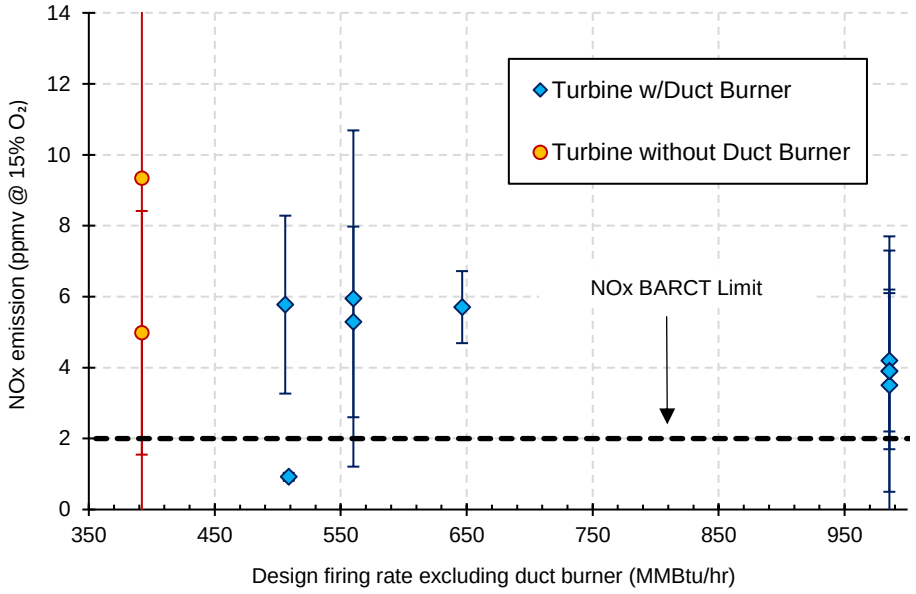
NEC recommends an averaging time of 24 hours.

The major control technology configuration for NOx in gas turbines is a combination of SCR and modern combustion technology, such as Dry Low NOx (DLN) combustors. Depending on the application, modern DLN combustors can achieve between 9 and 25 pppmv NOx emissions from gas turbine systems.[44] Gas turbines in the District operate with NOx levels less than 20 ppmv, most of them also include duct burners, see Figure 4.5-1. Gas turbines in the District are equipped with SCRs. Some SCR designs (most likely newer designs) may provide for the addition of about 50% more catalyst. With the use of recently developed modern catalysts, there is a high probability that the 2 ppmv level can be achieved by adding catalyst in existing SCRs. However, NEC only has limited information on the design and operating capability of the District's gas turbines. With catalyst modification and additions it is technically feasible that most gas turbines can achieve the 2 ppmv NOx BARCT limit.

Based on similar arguments presented in Section 4.1.1, NEC recommends the averaging time be extended to 24 hours.

[44] https://www.ge.com/content/dam/gepower-pgdp/global/en_US/documents/service/gas%20turbine%20services/9fa-dry-low-nox-2-point-6-plus-fact-sheet.pdf

Figure 4.5-1: NOx emissions from existing gas turbines in the District. Data points represent the average value and bars represent 2 standard deviations. Hourly data over 1 year of representative operation was used.



4.6 Coke Calciner

Table 4.6-1: NOx BARCT limits for Coke Calciner under proposed Rule 1109.1 from SCAQMD

Refinery Equipment Category	No. of Units in Category	Proposed BARCT Limit (ppm)	Corrected O_2%	Proposed Averaging Time	2017 NOx Emissions (tpd)	Cost-Effectiveness
Other Categories						
Coke Calciner						
Kiln/Pyroscrubber	2	5	3	365 day	0.71	$23,000
		10		7 day		

Combustion modifications will be difficult to implement on the Coke Calciner unit and will not provide a high level of NOx reduction if implemented. Minimum operating temperature in the Pyroscrubber afterburner is > 2,100°F (permit requirement for VOC destruction) which limits options to cool the flame and reduce thermal NOx formation. The Pyroscrubber afterburner is an adiabatic chamber and a lack of cold plane surface area means staged combustion and IFGR are not applicable to limit Thermal NOx formation. The adiabatic chamber is too hot for SNCR to provide any realistic NOx reduction. Viable solutions will have to deal with NOx downstream of the combustor (i.e. end-of-pipe solution).[9]

The proposed NOx BARCT limit of 5 ppmv means SCR will be required to achieve a NOx reduction of 92% (current NOx inlet concentration to the SCR unit is ~65 ppmv).

92% NOx reduction is achievable across a single SCR catalyst bed with good mixing at the preferred operating temperature range of 650 to 750°F. However, locating the SCR within this optimal temperature window is very difficult from a retrofit perspective and considerations may be required for low temperature SCR or duct burners to reheat the flue gas.

Other options that have been considered for NOx control with this application include LoTOx and UltraCat.[9] One important factor when considering the available options is plot space:

> "*One of the important conclusions of the NEC 2010 SOx RECLAIM report is that calciner space availability is very tight, and most of the equipment would have to be built elevated above the road used for coke loading/unloading access.*"[35]

NEC believes the technology that can reliably meet the 5 vppm NOx BARCT limit consistently for the Coke Calciner will be SCR.

The Coke Calciner has received a lot of attention and numerous cost estimates have been generated and reviewed for this particular unit.[9] NEC are in agreement with the proposed averaging time based on a 7 day average of 10 ppmv due to process and feed variations, and a 365 day average of 5 ppmv.

4.7 SRU TG (Sulfur Recovery Unit Tail Gas) Incinerators, Flares and Thermal Oxidizers

Table 4.7-1: NOx BARCT limits for SRU TG incinerators and thermal oxidizers under proposed Rule 1109.1 from SCAQMD

Refinery Equipment Category	No. of Units in Category	Proposed BARCT Limit (ppm)	Corrected O_2%	Proposed Averaging Time	2017 NOx Emissions (tpd)	Cost-Effectiveness
Other Categories						
SRU/TG Incinerators						
Incinerators	16	30	3	8 hour #	0.427	$39,000
Stack Heaters	3					
Flares & Thermal Ox.						
Afterburners, Vapor Incinerators, and Thermal Oxidizers	13	20	3	3 hour	0.048	$4,000
Open Ground Flares	1	Low Use (<20hrs)	3			$310,000

NEC recommends an averaging time of 24 hours.

SRUs accept H_2S rich gas from refinery sources for conversion into elemental sulfur through the Claus process. This mixed feed also contains precursor species like NH_3 and HCN, which enters a high temperature combustor (2,000 to 2,600°F) to convert H_2S into SO_2, SO_3 and and S_2. Retrofitting commercially available ULNBs into the SRU combustor will have minimal impact on the conversion of NH_3 and HCN to NOx (Fuel NOx), particularly at the high temperature the combustor operates at. Another complicating factor is the SRU combustor is typically an adiabatic chamber that does not contain cold plane surface area to actively cool the flue gas. The SRU combustor is too hot for SNCR to provide any realistic NOx reduction.

Fuel NOx and Thermal NOx formed in the SRU combustor continues with the flue gas through the Claus Plant and ends up leaving the last sulfur condenser as tail gas. The amount of tail gas and the composition of the tail gas leaving the last sulfur condenser and entering the SRU TG incinerator varies over time making it unlikely that there is any effective means of designing an ULNB to consistently achieve low NOx emission levels at the SRU TG incinerator, particularly when NOx is forming in the upstream SRU combustor. Commercially available ULNBs will provide little to no additional NOx reduction at the SRU TG incinerator. These units typically run at high excess air to ensure complete combustion and do not operate at temperatures where Thermal NOx formation is significant.[45]

Flue gas leaving the SRU TG incinerator contains elevated levels of SO_2 and SO_3. If the catalyst in a downstream SCR contains Vanadium some of the SO_2 will form SO_3 which can produce a plume of H_2SO_4 at the stack. Another concern is ABS formation in the presence of NH_3 and SO_3, which can foul SCR catalyst through capillary condensation in the pores. SCR is not a reliable solution for NOx control downstream of the SRU TG incinerator.

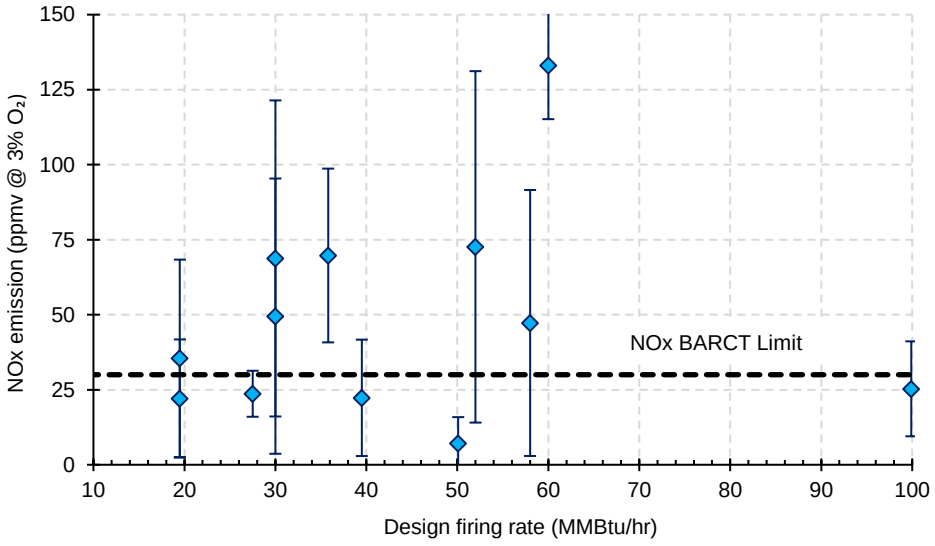
[45] https://www.zeeco.com/incinerators/incinerators-therm-ox-sulfur-tail-gas

If a wet scrubber is present downstream of the SRU TG incinerator to remove SOx species then LoTOx is an option.

Most of the existing SRU TG incinerators in the District are operating in the 75 ppmv range or less for NOx, see Figure 4.7-1. Seven existing SRUs are already achieving sub-30 ppmv NOx emissions using existing burner technology. An advanced, custom designed burner solution like that provided by John Zink for sulfuric acid plants and thermal oxidizers is the only cost effective solution for SRU systems to control NOx emissions. NEC are in agreement with the 30 ppmv NOx BARCT limit presented in Table 4.7-1 based on an advanced burner upgrade. Precursor species conversion to Fuel NOx may factor into the minimum achievable NOx emission level in some cases.

NEC recommends the averaging time be extended to 24 hours. The ability to diagnose an abnormal operational problem and take the necessary corrective action(s) before an exceedance occurs will be similar whether an SCR is installed or not as discussed in Section 4.1.1.

Figure 4.7-1: NOx emissions from SRU TG incinerators in the District. Data points represent average value and bars represent 2 standard deviations. Hourly data over 1 year of representative operation used.



While there are products available that can minimize NOx formation in thermal oxidizers and incinerators, these technologies are difficult to retrofit on existing units. High temperatures are required to achieve regulated destruction levels for criteria pollutants and advanced, custom designed combustion systems are the only practical solution to achieve low NOx emissions. CFD results have shown the key to low NOx operation in thermal oxidizers and incinerators is to improve the mixing and stage the introduction of fuel and air to maintain the flame as cool and as uniform as possible while still achieving the temperature required to thermally destroy criteria pollutants.[46]

NEC are in agreement with a NOx BARCT limit of 20 ppmv for afterburners, vapor incinerators and thermal oxidizers. As mentioned earlier, there are products available that can minimize NOx formation in thermal oxidizers

[46] NEC discussions with Zeeco on 11/6/2019 (project note 19-9009-009)

and incinerators but these technologies are difficult to retrofit on existing units. If NOx control technologies need to be implemented then NEC would expect the most cost-effective option to be an upgrade of the burner/combustor. These units are not expected to have a CEMS and 3 hours is an appropriate averaging time for source testing based on discussions presented in Section 4.1.1.