SOUTH COAST AIR QUALITY MANAGEMENT DISTRICT RULE 1109.1 STUDY FINAL REPORT

Prepared for

South Coast Air Quality Management District Diamond Bar, California 91765

Prepared by

Fossil Energy Research Corporation Laguna Hills, California 92653

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Fossil Energy Research Corp. 23342-C South Pointe Drive, Laguna Hills, California 92653 Telephone: (949) 859-4466 Fax: (949) 859-7916

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1 INTRODUCTION

South Coast AQMD Proposed Rule 1109.1 for NO_x emissions control will replace RECLAIM¹ for refineries and set Best Available Retrofit Control Technology (BARCT) NO_x emission limits for specific classes of refinery equipment, in contrast to RECLAIM's market-based system approach.

A number of NO_x control technologies are expected to play a role in meeting the new BARCT limits. Depending on the source category and heat input, the primary technologies are expected to be "Low" and "Ultra Low" NO_x burners (LNB and ULNB, respectively) and Selective Catalytic Reduction (SCR). Other technologies that may play a role on selective equipment types are LoTOx[™] (ozone based wet scrubber) by Linde and UltraCat[™] (catalytic filters) by Tri-Mer.

The objective of this project is to conduct a technical feasibility study and evaluate costs of deploying LNB, ULNB, or SCR to achieve various NO_x emissions levels for the various classes of refinery equipment. The approach employed in-house knowledge and recent supplier data with site characteristics acquired during on-site visits and through reviews of process equipment at major Southern California refineries. As part of this approach, FERCo reviewed and recommended changes to the cost estimating procedure employed by South Coast AQMD staff in their assessment of NO_x control cost.

The objective was carried out recognizing unique features of refinery operation, as communicated to South Coast AQMD staff by refinery stakeholders during the Working Group Meetings and site visits. These unique issues include:

- Implementation timing given that typical maintenance turnarounds take place every 5 years, and that planning for acquisition of both capital and construction labor are concluded at least 2 years prior to the event.
- Space can be limited in a refinery due to adjacent equipment and the need for maintenance access roadways and equipment staging areas. SCR reactors and ancillary equipment require adequate space for installation. These space limitations may require some creative engineering and can have an impact on retrofit costs.
- NO_x averaging times to accommodate the anticipated variable NO_x outlet values, when attempting to meet a low BARCT limit.
- Generation of particulate matter due to residual NH₃ from SCR and concentrations of sulfur compounds in the flue gas from the combustion of refinery fuel gas.

This report is comprised of six sections, addressing the following topics:

¹ Regional Clean Air Incentives Market (RECLAIM). See http://www.aqmd.gov/home/programs/business/business-detail?title=reclaim.

- Section 2: Overview of Refinery Equipment
- Section 3: NO_x Control Technologies (LNB/ULNB, SCR)
- Section 4: NO_x Control Costs
- Section 5 Observations from Refinery Site Visits
- Section 6 Conclusions

BACKGROUND: RELEVANT HOST EQUIPMENT

Section 2 presents background information overviewing different NO_x emitting sources in a refinery, and describes the constraints that govern the quantity of NO_x emissions during refinery operation, maintenance, and feasibility of various control technologies.

2.1 Refinery Overview

The NO_x-emitting sources in a refinery are characterized by application, heat input, and fuel type (natural gas or refinery gas). Figure 2-1 shows a simplified refinery flowsheet of the refinery process. Heaters and boilers represent two of the classes of refinery equipment that are Major sources of NO_x emissions



Simplified Refinery Diagram

Figure 2-1. Simplified Refinery Process Flowsheet²

² Refinery Outages: Description and Potential Impact on Petroleum Product Prices, Energy Information agency, Office of Oil and Gas, March, 2007. Available at https://www.eia.gov/analysis/requests/2007/SROOG200701.pdf

A typical refinery has dozens of such units, representing a wide variety of processing capability in terms of Heat Input (MMBtu/hr). Cumulatively, the category of boilers/heaters represents a significant source of refinery NO_x emissions.

Other categories of sources can also be major contributors to refinery-wide NO_x emissions. These categories include Fluid Catalytic Cracking (FCC) units, gas turbines, and Sulfur Recovery Unit/Tail Gas Incinerators (SRU/TG). As shown in Figure 2-1, the FCC is central to refinery operation, while the significance of the SRU/TG (not shown in Figure 2-1) varies with the type of crude material being processed. The main function of the SRU/TG is to oxidize H₂S to SO₂ with subsequent recovery of the sulfur as elemental sulfur.

Many refineries employ on-site electrical power generation to support refinery operation, utilizing conventional gas turbines deployed in combined cycle configurations. These power generating units generate NO_x , although typically are among the lowest emitters it terms of concentration but can be a major source on a tons per year basis.

A brief discussion of each of these categories is presented below.

2.2 Equipment Type

The major categories of process equipment are briefly discussed in this section: Boiler/Heaters, Fluid Catalytic Cracker (FCC) unit, SRU/TG unit, and the gas turbine. An assessment of the coke calciner, thermal oxidizers, and internal combustion engine category was not conducted, therefore they are not included in this report.

2.2.1 Boiler/Heaters

Fired heaters are devices that employ a radiant section where fuel combustion and radiant heat transfer occurs, followed by a convection section which contain a series of tubes used to preheat process fluid by convection. The radiant section can also be used as heat exchangers that generate steam in certain applications.

2.2.1a Boilers

Boilers in refineries are similar to boilers used in other industrial applications utilizing natural gas fuels. These typically use forced draft burners, and are amenable to both combustion controls (LNB, ULNB, Flue Gas Recirculation (FGR,) and SCR).

2.2.1b Heaters

There are a variety of heater designs used in the refinery industry. A large number are of a cylindered design with multiple burners located on the floor of the heater, firing refinery gas, or natural gas vertically upward. The majority of these heaters operate in a natural draft configuration. Figure 2-2 shows a typical natural draft heater arrangement.



Figure 2-2. Typical Natural Draft Refinery Heater Arrangement

The combustion process in these units is controlled by conventional burners that control the mixing of air and fuel, with the primary objective to maximize fuel utilization within the physical dimensions of the radiant section or firebox while distributing heat in a manner that supports refinery operation. As will be discussed in Section 3, the combustion process and generated NO_x can be reduced by LNB or ULNB technology.

2.2.2 Fluid Catalytic Cracking (FCC) Unit

The Fluid Catalytic Cracking Unit (FCC) is an important refinery process used to convert high boiling high molecular weight hydrocarbon material to lighter molecular weight products. This is done using a catalytic process. A byproduct of this process is a carbonaceous coke product. NO_x is produced in the FCC unit when this coke is burned off. Because of this solid coke combustion process, NO_x reduction using low or ultra low NO_x burners is not feasible. NO_x reduction from FCC units will require post-combustion technologies; SCR, LoTOxTM, catalytic filters (Ultra Cat), etc.

The FCC unit is one of the largest NO_x source in a refinery.

2.2.3 Sulfur Recovery Unit/Tail Gas Incinerator (SRU/TG)

The SRU/TG generates flue gas from the combustion of sulfur containing byproduct compounds that contain hydrogen sulfide (H₂S), carbonic sulfide (COS), and other sulfur-containing

compounds. The key role of a SRU/TG unit, shown in Figure 2-3, is to convert, or oxidize, various sulfur-containing compounds into sulfur dioxide (SO₂), a fraction of which will be further oxidized to sulfur trioxide (SO₃). NO_x is formed during this oxidation process. The oxidized sulfur is then recovered as elemental sulfur.



Figure 2-3. Sulfur Recovery Unit/Tail Gas Oxidizer

There are various means to reduce NO_x emissions from SRU/TG incinerators, including low or ultra low NO_x burners. However, such NO_x control measures are typically limited in their ability to reduce NO_x by more than 10-20%.³ Greater NO_x reductions can be achieved from the SRU/TG units using post-combustion NO_x control like SCR.

2.2.4 Gas Turbine/Combined Cycle

Gas turbines operating in combined cycle duty emit NO_x based on the design of the gas turbine combustor. As applied in combined cycle duty, SCR can be utilized to reduce NO_x emissions by placing catalyst in the open gas flow passages of the heat recovery steam generator (HRSG). Figure 2-4 shows a gas turbine equipped with a HRSG for the arrangement of gas flow from the gas turbine to the HRSG (right-to-left). These gas turbine/combined cycle units are widely used in the electric power industry.

SCR is installed within the Heat Recovery Steam Generator (HRSG) equipment to control NOx emissions.

³ Pickard, P., Sulfur Tail Gas Thermal Oxidizer Systems, Callidus Technologies, July 2017, available at https://refiningcommunity.com/wp-content/uploads/2017/07/Sulfur-Tail-Gas-Thermal-Oxidizer-Systems-Pickard-Callidus-Technologies-SRU-League-City-2010.pdf.



Figure 2-4. Gas Turbine with Heat Recovery Steam Generator

2.3 Fuel Type

The gaseous fuel used in a refinery varies significantly – ranging from either pipeline quality natural gas to the byproduct gas that is generated as part of refinery operations (refinery gas). Depending on the source size, duty, and location within the refinery, either of these two source gases, or a blend of both, can be used.

Table 2-1 presents an example comparing refinery gas and pipeline quality natural gas (mole percent basis). For the example presented in Table 2-1, natural gas is almost exclusively methane, while for refinery gas methane comprises less than 1/3 of the total product; about the same as hydrogen. Byproduct gas can contain higher-order carbon compounds (denoted in the table as C2+ paraffins). In the refinery gas example shown in Table 2-1, these higher order hydrocarbons are almost of the same level as the methane.

Table 2-1 shows one example of refinery gas composition, but it should be noted that composition can vary significantly depending on the crude oil being processed. Further, refinery fuel gas can also vary with time, hourly, daily, depending on the material being processed.

•	-					
Table 1: Typical Natural Gas and Refinery Gas						
Compositions						
Name	Refinery Gas	Natural Gas				
	Mol %	Mol %				
Hydrogen	28.00	-				
Methane	28.00	95.00				
C2+ parafins	24.00	3.50				
Olefins	10.00	0.00				
Nitrogen	3.50	1.00				
Carbon Dioxide	3.00	0.50				
Carbon Monoxide	3.50	0.00				
Total	100.00	100.00				
Sulfur ppm	25-250	5				

Table 2-1. Typical Natural Gas and Refinery Gas Composition

2.4 Operations

Refinery operation requires continuous processing of the crude oil feedstock for extended periods, with minimal interruption, over a time period of as long as 5 years. Figure 2-5 shows the percent utilization of refining operating capacity, in terms of a 4-week average, from 1995 through most of 2019 for refiners in the West Coast. As can be seen, near full-capacity operation is the norm and "downtime" or outages are negligible. Most of the major maintenance and upgrades are conducted during the "turnaround" at time intervals that can be as long as 5 years (and in some instances longer).



Figure 2-5. Four-Week Refinery Percent Utilization: West Coast Refineries⁴

⁴ https://www.eia.gov/dnav/pet/hist/LeafHandler.ashx?n=PET&s=WPULEUS3&f=4.

Turnarounds are planned periodic shutdowns of either the entire or key portions of a refinery for inspection, repair, general maintenance, and installation of new equipment. These periodic events are the best opportunity to conduct such activities. With regard to installation of equipment needed to comply with Proposed Rule 1109.1, this will need to be incorporated into the turnaround schedules.

2.5 Factors Affecting NO_x Control Cost

The factors that affect installation costs – and the analysis that defines the evaluated cost per ton of NO_x removed are reviewed in this section.

2.5.1 Components of Incurred Technology Cost

Equipment to reduce NO_x emissions is comprised of direct components that reduce the NO_x content, and indirect components that, though not directly affecting NO_x removal, enable operation of equipment to do so. Any analysis of costs must first define the scope of activities.

Scope

The cost of process equipment, both capital and operating, should be clarified in terms of contribution to the NO_x compliance project. For example, upgrade of the instrumentation and control system to enable an SCR reactor to effectively "load follow" a refining process is accountable to the NO_x control budget. Also, an SCR reactor will likely require additional flue gas fan and auxiliary power to prompt flue gas through the reactor which are both accountable to the NO_x control budget. Not all equipment upgrades can be completely assigned to the NO_x project budget. For example, several detailed studies of SCR reactor auxiliary power demand identified the need to upgrade the on-site electric power supply. These upgrade costs would be incorporated into the SCR system costs, unless a portion of the power is otherwise utilized or provides some benefit to another process or use, in which case the costs would be shared. Similarly, any improvement to the instrumentation and refining control system that benefits other aspects of operation should be accounted towards another budget.

A NO_x control project scope will also include equipment or process steps that affect byproducts from the process. For SCR, these byproducts typically include residual NH₃, sulfur trioxide (SO₃) from the oxidation of SO₂; and perhaps most importantly the products of reaction between these two species known as secondary particulate matter. During site visits for this project, all refinery owners noted that reductions in the sulfur content of refinery fuel gas will be required to limit particulate matter production attributable to SCR. The issue of whether the significant investment in additional sulfur-removing equipment is accounted for in the NO_x control budget was discussed extensively.

Process Equipment

Process equipment is categorized in terms of providing direct or indirect functions.

For LNB, direct process equipment are the burners, air registers, fuel oil or gas injector tips, and any instrumentation or measurement equipment to monitor or adjust operation. The indirect

equipment or components are changes to the "windbox" or combustion air ductwork to assure proper combustion air flow, or to the fuel delivery system to assure adequate gas pressure.

For SCR, direct process equipment includes the catalyst, reactor, ductwork to accommodate the reactor into the gas flow path, reagent system, and process controls.

Indirect process equipment for SCR systems can include changes to, replacement of, or installation of new forced, or induced draft, gas fans to overcome the additional pressure drop caused by the reactor, or additional electrical supply equipment to support the SCR system.

Labor/Leased Installation Equipment

The cost of labor and leased equipment to install direct and indirect process equipment can be significant, and can exceed the cost of process equipment. The direct and indirect process equipment must be relocated from delivery point to installation site with cranes and other heavy-equipment moving apparatus, which require considerable labor for support. A principle factor determining the indirect installation cost is the complexity of the site; some sites offer relatively "open" access while others are congested sites requiring extensive installation duties.

Figure 2-6 is an example of a relatively open site, in which direct and indirect process equipment can be delivered adjacent to the unit, minimizing installation duties. Conversely, Figure 2-7 represents a crowded site, with complex installation. The site's distance from the main access road and the intervening pipe racks require multiple "pick-ups" or actions of the crane, forcing relocating equipment to execute several discrete steps.

A final factor that affects the costs is site's underground conditions. In both the electric utility industry and at refining sites, there are "legacy" underground barriers that complicate installing foundations, typically for routing process water or power lines. Discussions with refinery staff indicated that it is rare to excavate for foundations without incurring some type of obstruction that, although manageable, imposes a delay and additional cost. In addition, some of the Southern California refineries are located near the coast. This could entail substantial foundation work due to the nature of the soil.

Consequently, installation cost for NO_x controls, particularly for gas treatment equipment such as SCR, can significantly exceed that of NO_x control equipment. One method to quantify this trend is to consider the ratio of installation cost to that of NO_x control equipment, the former accounts for the costs of all indirect process equipment, labor, and leased equipment for installation, and the latter solely accounts for the costs of NO_x control equipment. Figure 2-8 presents this ratio for a variety of gas treatment processes in the electric utility and refining industry. These projects include retrofit of SCR for coal-fired power plants, and retrofit of particulate and flue gas desulfurization equipment for such plants. Also shown is this cost ratio for retrofit of SCR to a refinery heater/boiler within the South Coast AQMD, as determined by a detailed engineering study conducted for that refinery. As can be seen in Figure 2-8, the total costs exceed the process equipment costs by a factor of at least 2.5 in both the electric utility industry and refineries.



Figure 2-6. Relatively Open Access: Refinery Heater



Figure 2-7. Relatively Congensted Access: Three Heaters



Figure 2-8. Ratio of Indirect and Construction Cost to Process Equipment Cost: Various Flue Gas Treatment Projects

NO_X CONTROL OPTIONS

3.1 Ultra Low NO_x Burners

Ultra Low NO_x Burners (ULNB) are burners with NO_x emissions less than 10 ppm when firing refinery gas. Burners achieving these NO_x levels are currently in the prototype or demonstration stage. Previously, ULNB's were considered capable of providing NO_x levels on the order of 20 ppm while firing natural gas. Retrofit burners must also comply with API Standard 535 and 560.

Currently, two vendors have stated that they will be offering UNLBs with less than 10 ppm NO_x emissions while firing refinery gas. These vendors are ClearSign and John Zink Hamworthy. Their ULNB specs are discussed below.

ClearSign

ClearSign's current offering in the ULNB category is its Core[™] burner. The Core[™] burner stabilizes the flame on a ceramic element. A continuous internal pilot provides start up fuel and can also act as a flame stabilizer once the main gas valve opens. The burner is shown schematically in Figure 3-1.



Figure 3-1. ClearSign Core Burner Schematic

ClearSign installed their earlier design burner on two vertical cylindrical refinery heaters in April 2016 and October 2016. The second installation was at the Tricor asphalt plant in Bakersfield, California. The design firing rate for the burner was 8 MMBtu/hr. NO_x emissions were in the range of 4.0 to 5.5 ppm_c.

The continuous pilot core technology burners were first installed in June 2019, with a rated heat input of 15 MMBTU/hr. Reported emissions were <6 $ppm_c NO_x$ and < 5 $ppm_c CO$. ClearSign has teamed with Zeeco to market and fabricate this ULNB. A full scale demonstation of this burner at a Southern California site is expected in early 2021.

John Zink Hamworthy

John Zink Hamworthy's ULNB offering is the SOLEX burner, which is shown schematically in Figure 3-2. This burner is under development. The burner comprises two zones; an AIRmixTM and COOLmixTM zone. The AIRmixTM zone is a controlled fuel-air ratio combustion zone that is anchored within the burner tile. The COOLmaxTM zone incorporates staged fuel diluted by furnace gases.



Figure 3-2. Schematic of John Zink Hamworthy SOLEX Burner

The SOLEX burner has a single piece burner tile. Its tips are individually removable. Air is supplied to a single point, while two fuel zones are required. The burners are sized for heat release rates ranging from 1 to 20 MMBtu/hr. The burner is compatible with pilots, UV scanners, and igniters.

Pilot-scale studies, at John Zink Hamworthy's facility, have demonstrated 5 ppm NO_x emissions with very low CO levels, while firing a simulated refinery fuel gas. John Zink Hamworthy claims that NO_x emissions remain steady over a range of fuel compositions containing up to 75% hydrogen (H₂). They also claim that NO_x emissions are not affected by air preheat, furnace temperature, or firebox heat density.

Flame lengths for the SOLEX burner are low; less than half of the length of their previous ULNB offerings. Both round and flat flame options will be available.

The NO_x performance described above was achieved in John Zink Hamworthy's pilot facility. No field data were available at the time this report was prepared. A field demonstration of the SOLEX burners is tentatively scheduled early in 2021.

3.2 SCR

Selective Catalytic Reduction (SCR) involve passing flue gas containing NO_x over a catalytic surface following the introduction of either ammonia or urea. The resulting products are water (H₂O) and nitrogen (N₂) (see Figure 3-3). The primary SCR reactions are shown below.





Figure 3-3. Overview of the SCR Process

In most instances, NO comprises the majority of the NO_x, so reaction (1) dominates. Reactions (3) and (4) occur in gases where NO₂ is a majority of the NO_x. To allow these reactions to occur at temperatures between 400 and 900°F (200 - 480°C), a catalyst is used. Next, we will briefly review important SCR parameters.

1) Catalyst Activity, K(m/hr)

Catalyst activity is primarily a property of the material. Adding more vanadium to the catalyst will also increase its activity. Catalyst geometry and gas velocity can also affect activity.

2) Specific Surface Area, A_{sp} (m²/m³)

The A_{sp} is the amount of catalyst surface per volume of catalyst. A smaller catalyst pitch means more surface area.

3) Catalyst volume, V_{cat} (m³)

The volume of catalyst in the reactor.

4) Space Velocity, SV (sec⁻¹)

Space velocity characterizes the size of the SCR reactor and is defined as the ratio of flue gas flow per unit volume of catalyst:

 $SV = Q_{(stp)}/V_{cat}$

Where $Q_{(stp)}$ is the gas flow rate at standard temperature and pressure.

5) Area Velocity, Av

Area velocity is the amount of catalyst surface per unit of flue gas, and is defined as:

 $A_V = Q_{(stp)}/(V_{cat} \times A_{sp})$

6) Reactor Potential, RP

Reactor potential is a key parameter that defines SCR performance (i.e., ΔNO_x and NH_3 slip) and is a function of initial NO_x , ΔNO_x , and NH_3 slip. Reactor potential is defined as:

$$RP = \frac{K A_{sp} V_{cat}}{Q_{fg}}$$

This is basically the catalyst activity K, times the total catalyst surface area that the flue gas contacts flowing through the catalyst (K AspVcat) divided by the flue gas flow rate. The definition of the individual parameters are discussed above.

Next, the steps for designing an SCR reactor are reviewed. The first step is to establish the performance requirements, including the required NO_x reduction and ammonia slip. Second, catalyst replacement or addition intervals should be determined. For refinery applications, this is likely to be on the order of five (5) years to coincide with scheduled turnarounds. Third, determine the catalyst deactivation rate (K/Ko versus time) for the specific flue gas. For natural gas, a deactivation rate of 2% per 10,000 hours is typical. This could be expected to increase to nominally 4% per 10,000 hours for refinery gas. One catalyst vendor suggests that an end-of-

life K/Ko of 0.72 be used for typical refinery applications. Where chrome poisoning is a possibility, the vendor suggests that a K/Ko of 0.58 be used.

Next, the minimum reactor potential needed to achieve the NO_x reduction and NH_3 slip targets must be calculated. This calculation is based on end-of-life conditions.

A margin of safety must then be added to account for deposition of solids on the catalyst surface (fouling) restricting the flue gas flow through the catalyst (minimal on gas-fired units) as well as velocity and NH_3/NO_x maldistributions. The catalyst channel opening is then selected, taking into account pressure drop and deposition considerations. Finally, the required catalyst volume can then be determined.

There are other conditions that need to be addressed, particularly if high levels of NO_x reduction are required:

- Ammonia injection grid (AIG) design
- AIG Tuning

The AIG design needs to take into consideration of the level of NO_x reduction required. Higher NO_x reduction requirements require a more uniform NH₃/NO_x distribution entering the catalyst. This, in turn, means a more complex AIG design in terms of adjustability of the NH₃/NO_x ratio over the surface of the catalyst. The measure of AIG tuning effectiveness is the RMS. The RMS is defined as the standard deviation of the measured NH₃/NO_x ratio at each sample point divided by the average NH₃/NO_x ratio, expressed as a percentage. Or, in equation form,

RMS = 100 x (NH₃/NO_x)_{std dev} / (NH₃/NO_x)_{avg}

Figure 3-5 shows how RMS affects SCR performance for both a new catalyst and the same catalyst near end-of-life using a gas turbine as an example. In this example, a NO_x reduction between 90 and 95% is required, along with NH₃ slip less than 5 ppm. This target area is shown by the green boxes on the graphs. For a new catalyst (the upper plot), it shows that 90% deNO_x can be achieved for RMS values up to about 25%. Note, however, that for the 25% RMS case, the NH₃ slip is nearly at the 5 ppm level at new conditions. If 95% deNO_x is required, the RMS must be about 15% or less. Next, consider the results for the same catalyst near its end-of-life. First, note that it can no longer provide 95% deNO_x with 5 ppm NH₃ slip, regardless of the RMS. It can achieve 90% deNO_x, with RMS values less than 15%, albeit with higher NH₃ slip values than when new.

Next, SCR performance was calculated for a refinery heater using the following parameters:

- Flue gas flow rate = 397,500 lb/hr
- Inlet NO_x = 70 ppm
- Outlet NO_x = 2 ppm
- NH_3 slip = 5 ppm
- Flue gas temperature = 625°F



Figure 3-4. Example Calculation for NH₃/NO_x Distribution and AIG Tuning

Using these values gives a minimum reactor potential (RP_{min}) of 3.88. A design for a five year operating cycle while firing refinery gas might target K/Ko = 0.7 at end-of-life. This end-of-life is basically the interval between turn-arounds, not the life of the SCR. Most refineries will likely opt to replace SCR catalyst during a scheduled turn-around. This results in an initial new RP of 5.5. The corresponding catalyst volume for this example is then 10.2 cubic meters (m³). The examples that follow look at SCR performance for varying RMS values, both at system start up and at 20 percent of remaining catalyst life (i.e., 4 to 5 years in service). These calculations were performed using both the base catalyst volume and with an additional 50% catalyst volume (i.e., 15.3 m³).

Figure 3-6 shows the SCR performance with new catalyst. Two cases are shown; one for the design catalyst volume and one for the 150% of design volume. The plots show that an RMS of between 5% and 7.5% is needed to achieve 2 ppm outlet NO_x with the design catalyst volume with some margin in terms of NH_3 slip. With the increased catalyst volume, the required minimum RMS increases to about 7.5%. These calculations show that the extra catalyst has little impact on SCR performance when the system is new. This can be most easily seen by comparing the results obtained with a 10% RMS.



Figure 3-5. Example Heater SCR Performance with New Catalyst

Figure 3-6 shows the corresponding SCR performance when 80% of end-of-life RP is reached. This is equivalent to about 35,000 hours of operation. Cases for both the design catalyst volume and 150% design catalyst volume are shown. With the design catalyst volume, the calculations show that an RMS of about 5% is needed to meet the emissions targets. While an RMS of 7.5% allowed compliance when the catalyst was new, it does not allow compliance as the catalyst reaches 80% of its life. In comparison, with the 150% design catalyst volume, the RMS required to meet the emission targets is now 7.5% with a fair amount of margin remaining in terms of NH₃ slip.



Figure 3-6. Example Heater SCR Performance with Catalyst at 80% End-of-Life

3.2.1 Conventional Design Basis

A conventional SCR design for NO_x compliance would likely utilize low NO_x burners (LNB) to minimize the NO_x going into the SCR. This is important since as inlet NO_x increases, the required level of NO_x reduction also increases. While designing an SCR for 90% NO_x reduction is relatively straightforward, requiring an SCR system to provide 95% (or more) NO_x reduction

requires a much more sophisticated system in terms of catalyst volume and NH_3/NO_x distribution entering the catalyst (i.e., AIG design).

The NH_3 slip limit also must be defined so that the minimum RP can be determined for the unit. Note that the NH_3 slip limit must be defined as part of the SCR design. Minimizing NH_3 slip is important both to minimize NH_3 slip (and resulting operating costs) as well as limiting the potential for byproduct emissions.

Equally important is the AIG design and its ability to produce the required NH_3/NO_x distribution (RMS) entering the catalyst. In fact, the AIG design and the resulting ability to tune the AIG can be as important as the catalyst volume. AIG design is becoming more important as emissions limits decrease. Catalyst performance guarantees are typically based on a stated NH_3/NO_x uniformity (RMS). The RMS is determined by the AIG design and its adjustability, thus AIG design directly impacts SCR system performance (and performance guarantees).

The simplest AIG design (see Figure 3-7) incorporates lances entering from a single wall of the duct. They can be oriented either horizontally (as shown) or vertically. If there are no valves to adjust the flow to the individual lances, the best RMS one could expect would be about 17%. If valves are added, the best RMS that could be achieved would likely be somewhat above 10%. The problem with this design is that the ammonia can only be adjusted in one direction. For the example shown, the ammonia can only be increased or decreased vertically up and down the catalyst surface, not side to side.

Another AIG design is shown in Figure 3-8. In this case, the ammonia can be adjusted vertically, as well as between the left and right sides. The limitation of this design is that it can only adjust the ammonia flow in two zones in the horizontal direction. Often times, this is not enough as the ammonia flow to the sides needs to be adjusted independently of the ammonia flow to the duct center. A typical RMS for this type of AIG is similar to the AIG grid shown in Figure 3-7 (i.e., approximately 10%).



Figure 3-7. AIG with Single Lances Oriented in One Direction



Figure 3-8. AIG with Two Rows of Lances

Figure 3-9 shows AIG designs that can provide RMS values on the order of 5%. The design on the left is referred to as a cross-grid AIG. Lances oriented both horizontally and vertically allow the ammonia to be distributed in both directions. One of the limitations of the cross-grid design is that it is difficult to affect the ammonia flow to a single small area of the duct. The design shown on the right has lances entering from only one wall (in this example, the side wall) but divides the duct into three zones horizontally. The three horizontal zones, along with multiple vertical zones, seems to be the minimum needed to achieve RMS values in the 5% range.





Another approach, used primarily on gas turbines, is direct injection near the turbine exit where flue gas velocities are high and mixing good. This is shown in Figure 3-10, where direct ammonia injection is being used on a large gas turbine combined cycle system. In these systems, RMS values between 3 and 7% are achievable. This approach could be used in a vertical cylindrical heater where the flue gas is taken from near the top of the heater and directed to an SCR near grade. Injecting the reagent at the top of the duct leading to the SCR could provide similar results.



Aqueous ammonia injector (1 of 9)

Figure 3-10. Direct Injection for a Gas Turbine

Figure 3-11 shows the resulting NH_3/NO_x profiles following the tuning of the AIG on a gas turbine using direct injection (Figure 3-10). While the profile exhibits some vertical stratification, the calculated RMS was 2.7%. It should be noted that this is not a new concept. The City of Redding, in Northern California, has been using direct aqueous ammonia injection on 3 small gas turbines for years. More recently, they have installed direct urea injection systems on two 45 MW combined-cycle gas turbines.



Figure 3-11. Contour Plot of the Local NH₃/NO_x Ratio on a Gas Turbine Using Direct Injection

Another method of injection is injection upstream of a booster fan with the SCR reactor located downstream. The results of one such system, applied to a small (30 mmBtu/hr) industrial boiler, is shown in Figure 3-12. The plot shows the normalized NH_3/NO_x ratio plotted versus location. The resulting contour plot shown very little variation, as exhibited by the calculated RMS value of 2.7%.



RMS: 2.7%

Figure 3-12. NH₃/NO_x Profiles on a Small Industrial Boiler Utilizing Direct Injection for the SCR

Another concern in the AIG design is the sizing of the orifices on the individual lances. The holes must be designed so that there is sufficient pressure drop through them to evenly distribute the ammonia along the length of the lance. The importance of this is illustrated in Figure 3-13. In this case, the AIG lances enter the duct from the top. Note that the NO_x along the top of the duct is about 25 ppm, while it is only a few ppm at the bottom. The resulting RMS was 26.4%. This indicates that the majority of the ammonia is flowing out of the bottom of the lances, while much less flows out of the top. This maldistribution was entirely due to incorrectly sized orifices on the AIG lances.

3.2.1.1 NO_x, Residual NH₃ Targets

Currently, proposed NO_x emissions limit for a majority of the refinery units subject to Proposed Rule 1109.1 is 2 ppm. With many current NO_x emissions levels ranging from 70 to 30 ppm, NO_x reductions ranging from 93 to 97 percent will be required. While not impossible, attaining these levels of NO_x reduction will be challenging. Careful SCR design and frequent tuning of injected ammonia and flue gas will be required in all cases.

While no NH₃ slip levels are currently specified in the proposed rule, NH₃ slip levels of 5 ppm were mentioned at Rule 1109.1 Working Group Meeting #9 in December 2019 as the Best Available Control Technology that will be imposed during permitting. These slip levels should be achievable with proper SCR design.

3-12



Figure 3-13. Example of Maldistribution Due to Improperly Sized AIG Orifices SCR Outlet NO_x Concentrations, ppm

3.2.1.2 Byproduct Emissions

As mentioned above, NH_3 is a byproduct emission of the SCR process. SCR catalysts will also oxidize a portion of SO_2 in the flue gas to SO_3 . The amount of SO_2 oxidation varies with the catalyst formulation, the operating temperature and the initial SO_2 concentration. Reported SO_2 to SO_3 oxidation rates have ranged from 1% to more than 20%.

The primary concern here is the reaction between SO_3 and NH_3 to form either ammonium bisulfate or ammonium sulfate, as follows:

$NH_3 + SO_3 + H_2O \rightarrow NH_4HSO_4$ (ammonium bisulfate)	(1)
$2NH_3 + SO_3 + H_2O \rightarrow (NH_4)_2SO_4$ (ammonium sulfate)	(2)

These reactions generally take place at temperatures below 500°F, and can lead to fouling in some convective sections. These ammonia compounds can also be emitted as particulate matter (PM).

Based on this, reactions (1) and (2) are the primary concerns for ammonia-based PM emissions. Note that for ammonium bisulfate (ABS) (1), the PM is limited by the <u>smaller</u> of the NH₃ or SO₃ concentrations. Thus, if there were 4 ppm NH₃ and 1 ppm SO₃, the resulting ABS concentration would be limited to 1 ppm. Reducing the NH₃ from 4 ppm to 2 ppm would not change the resulting amount of ammonia bisulfate. It would still be 1 ppm as dictated by the

3-13

smaller of the NH_3 or SO_3 concentrations. The only thing that would happen is that the ammonium bisulfate would form at a lower temperature along the gas path.

3.2.2 Upgrading Existing SCR Reactors

Some of the units subject to Proposed Rule 1109.1 either have existing SCRs, or are in the process of installing SCRs to comply with the 2015 RECLAIM amendments or NO_x shave. The NO_x reduction performance of these systems is not well known. The question is what, if any, changes are required for these SCR systems to be brought into compliance with Proposed Rule 1109.1.

To evaluate the performance improvement potential of these existing SCRs, the SCR system design must be reviewed. This review would include gas flow design, inlet NO_x and control NO_x values, AIG design, SCR catalyst type and volume, and overall system layout. If available, AIG tuning test results should also be reviewed.

The first step is to perform SCR modeling. This will provide an overall indication of possible SCR performance. If this exercise shows that the system is capable of delivering performance at or near Proposed Rule 1109.1 limits, then only minor changes may be required.

If the calculations indicate that the SCR will not meet the Proposed Rule 1109.1 requirements, the catalyst volume should be assessed. If additional catalyst is required, the amount can be calculated. Depending on the change in volume, it may be necessary to redesign the reactor. Any increase in catalyst volume will also increase the system pressure drop. This can be calculated and compared to the system design. If it exceeds the design specifications, a fan upgrade (or new fan) may be necessary.

Changes may be required for the AIG as well. These changes may include any of the following changes:

- Resizing existing AIG orifices
- Redesigning AIG
- Adding flow control valves
- Moving AIG to different location
- Adding static mixers

All of these changes are relatively minor, involving at most piping modifications.

Overall, upgrading existing SCR systems to comply with Proposed Rule 1109.1 are estimated to cost between 10 and 35% of the cost of a new SCR. Since all of the SCR infrastructure is already in place, only minor modifications will likely be needed.

4

SELECTIVE CATALYTIC REDUCTION COST BASIS: EPA MODEL AND INDUSTRY SOURCES

This section addresses the basis for estimating the cost for deploying SCR NO_x reduction on refinery units. Both the EPA-sponsored SCR cost model and industry sources of cost inputs are addressed in this critique.

4.1 EPA Cost Model

The EPA for decades has developed and employed the Integrated Planning Model (IPM) to "analyze the projected impact of environmental policies on the electric power section".⁵ The EPA established the SCR cost prediction method by contracting with Sargent & Lundy Engineers (S&L) to develop a correlation of installed cost with various design and site features, derived from SCR installations at electric utility industry coal-fired power stations. The basis for this work was initially developed in 2008 and updated several times, most recently in 2017.⁶. These basic cost relationships developed by S&L are adopted within the model, as described in the model handbook.⁷

In perspective, the purpose of the IPM in general and of the SCR component is to assess the long-term, aggregate impacts of environmental legislation on an industry sector. The model is intended to provide an approximation of cost:

The cost-estimating methodology presented here provides a tool to estimate study level costs. Actual selection of the most cost-effective option should be based on a detailed engineering study and cost quotations from equipment suppliers.⁸

As per the preceding passage, the IPM documentation is replete with such statements; also highlighted by commenters.⁹ South Coast AQMD staff are aware of this limitation and have acknowledged the intended application is to approximate cost and not provide an estimate commensurate with that derived by a detailed engineering study. The cost-estimating procedure

⁵ https://www.epa.gov/airmarkets/clean-air-markets-power-sector-modeling.

⁶ IPM Model – Updates to Cost and Performance for APC Technologies: SCR Cost Development Methodology, Project 13527-001, January 2017. Hereafter 2017 IPM SCR Methodology.

⁷ EPA Cost Manual, Section 4 – NOx Controls, *Chapter 2, Selective Catalytic Reduction*, prepared by Sorrels, J.L. et. al., available at https://www.epa.gov/economic-and-cost-analysis-air-pollution-regulations/cost-reports-and-guidance-air-pollution.

⁸ Ibid. See Section 2.4 Cost Analysis.

⁹ Use of EPA SCR Cost Model to Estimate Refinery and Boiler Control costs and Cost-Effectiveness under SCAQMD Proposed Rule 1109.1, Refinery Equipment, Letter to Michael Krause from Bridget McCann, November 18, 2019.

developed by S&L can be interpreted as a "Class 4" study as defined by AACE International in their 2020 updated recommendation.¹⁰ Per this definition, the IPM deliverable is cost estimate of 80% confidence, which could be between 30% low to 50% high of that 80% confidence value.

Despite these limitations, exercising the EPA SCR Cost model can approximate NO_x control costs incurred by stakeholders, if the input equations developed for utility-scale and industrial boilers are replaced with terms reflecting refinery application. The model with these changes can provide value in understanding how variants of the proposed Rule 1109.1 affect compliance decisions. Complemented by actual incurred costs as reported by the refineries, the model can provide insight to policy decisions.

4.2 Capital Cost Changes: New Installations

There are substantial changes to the model and the inputs which South Coast AQMD staff have already initiated.

Capital cost estimates for SCR process equipment as estimated by members of the Western States Petroleum Association (WSPA) have been transmitted to South Coast AQMD staff and applied in the revised version of the SCR Cost Model. Specifically, WSPA reported capital cost estimates developed by members for SCR technology to comply with Rule 1109.1; such costs were developed to an "intermediate" or "preliminary" basis. This data has been collapsed into a correlation and imbedded into the SCR Cost Model. This version of the model was used as the basis for the cost evaluation presented by South Coast AQMD staff on December 12, 2019.¹¹

In addition, changes should be implemented to the catalyst volume specified by the SCR Cost Model to meet the stated NO_x and residual NH_3 limits. The impact of the change in catalyst volume and acquisition cost is small compared to the total cost of process, as will be discussed subsequently, as numerous factors other than catalyst volume determine installed SCR cost. However, the cost relationships in the present model do not accurately reflect the increase in catalyst volume that is required to lower NO_x emissions from 7 ppm to 5 ppm and ultimately to 2 ppm (at 2 or 5 ppm NH_3). This inaccuracy will distort operating cost as accurate catalyst replacement charges are not properly represented.

The role of catalyst volume on the installed cost for applications within a refinery will likely range from 5 - 10%. An increase in catalyst cost by 70%, as shown by the example in Table 4-1, will add not only additional catalyst volume but can increase the physical reactor size, supporting structural steel, and gas handling equipment to overcome the additional pressure drop. An additional layer of catalyst, if needed, can also require additional cleaning apparatus such as sootblowers or acoustic horns.

The role of catalyst volume on the variable operating cost for catalyst management will be in direct proportion to the change in catalyst volume; thus a 70% increase in catalyst volume (as to

¹⁰ Cost Estimate Classification System – As Applied in Engineering, Procurement, and Construction for the Process Industries, AACE Recommended Practices, Sample document 18R-97, August 7, 2020. Available at https://web.aacei.org/docs/default-source/toc/toc_18r-97.pdf?sfvrsn=4. Hereafter AACEI 2020 Classification.

¹¹ *Rule 1109.1 – NOx Emission Reduction for Refinery Equipment*, SCAQMD Working group meeting #9, December 12, 2019.

be illustrated in Table 4-1) will impose a 70% increase in the annualized cost for replacement catalyst. Recent studies have shown that catalyst costs account for nominally 5 percent of the total SCR system capital cost.

One shortcoming in the model appears to be the use of the same catalyst design, geometry, specific surface area, and "activity" for NO_x control regardless of the fuel. This is observed based on "exercising" the model and noting no change in catalyst regardless of whether natural gas, fuel oil or coal is the fuel. There is no documentation in either the spreadsheet or the manual that define the geometry of the catalyst; specifically catalyst volume to achieve a given NO_x and residual NH₃ outcome does not appear to change when fuel type is switched from coal to natural gas, suggesting catalyst of the same pitch and specific surface area is used. This is a clear shortcoming.

The estimates of catalyst volume for a given application appear to be inconsistent to those based on a state-of-art methodology to determine catalyst volume for natural gas firing based on discussions with catalyst suppliers. The differences in the two procedures is shown in Table 4-1, presenting results of an exercise for a conventional refinery boiler to determine the catalyst volume required to reduce NO_x from inlet values of 40 and 25 ppm to three outlet values - 7, 5, and 2 ppm. All NO_x reduction cases must meet a residual NH_3 limit of 5 ppm. Table 4-1 compares catalyst volume as determined by two means - the costing procedure imbedded in the EPA spreadsheet and an updated method using the reactor potential as derived from catalyst supplier's information.

Inlet NO _x	Outlet NO _x	Catalyst	EPA	Catalyst	Reactor
(ppm, at 5%	(ppm, at 5%	Volume, EPA	Procedure	Supplier-	Potential
O ₂)	O ₂)	Procedure	Percent	Derived	Percent
-	-	(m ³)	Catalyst	Reactor	Catalyst
			Volume	Potential,	Volume
			Increase	(m ³)	Increase
			from 7 ppm		from 7 ppm
40	7	14.2	-	14.5	-
40	5	14.8	4.6	17.4	19
40	2	15.8	11.4	24.6	70
25	7	12.7	-	11.5	-2
25	5	13.8	8	12.8	12
25	2	15.3	20	16.8	46

Table 4-1. Catalyst Volume to Achieve Three NOx Limits: EPA vs. Catalyst Suppliers Estimates¹

¹ 174 MBtu heater, inlet NO_x of 25 and 40 ppm, residual NH₃ of 2 ppm.

Table 4-1 shows the increase in catalyst volume using the EPA spreadsheet to lower NO_x from 7 ppm to 2 ppm is 11.4%, for an inlet NO_x value of either 40 or 25 ppm. To increase the NO_x reduction from 82.5% with an outlet NO_x level of 7 ppm to 95% in order to achieve an outlet NO_x level of 2 ppm requires an increase in catalyst volume by 11.4%. Starting at a lower inlet NO_x level of 25 ppm requires an increase in catalyst volume of 20% to go from 7 ppm to 2 ppm outlet NO_x concentration.

This increase in catalyst volume is significantly higher when calculated using the updated method derived from catalyst suppliers. Specifically, the increase in volume to lower NO_x outlet

emissions from 7 ppm to 2 ppm is 70%, for the inlet value of 40 ppm. The increase in volume to achieve the same reduction for an inlet value of 25 ppm is 46%. The increase in catalyst volume to achieve 2 ppm NO_x is notably higher using the updated method compared to that in the EPA spreadsheet. While it is worthwhile to improve the estimate of the required catalyst volume, the main impact will be in estimating operating costs assuming that the catalyst will be replaced during each turn around. In terms of SCR system cost, catalyst volume will have a lesser impact as catalyst cost is on the order of 5% of the overall SCR system costs.

4.3 Operating Cost Changes: New Installation

The following observations are presented in order for operating cost.

<u>Fixed Operating Costs</u>. Fixed operating costs are defined by maintenance activities, engineering evaluation, spare parts inventory, administration, and other actions required that are independent of the amount of process operating time. The Sargent & Lundy analysis developed a fixed operating cost basis from experience with coal-fired power stations, of which the largest component is 0.5% of total capital investment, incurred annually. To this estimate a second administrative charge is assigned, that equates 3% of the annual cost for one operator, and a further administrative charge of 0.006% of process capital. The value of 0.5% of capital is relatively low compared to analogous metrics for flue gas equipment as used in EPRI cost studies for power industry applications. Assigning 3% of operator duty translates into about 45 minutes of each day; this value corroborates with the experience of the authors in developing operating and maintenance guidelines for SCR in the power industry.

One fixed operations and maintenance (O&M) duty, critical for SCR targeting extremely low outlet NO_x emissions, is the "tuning" of the reagent injection grid (at intervals of one or two years). Achieving consistent NO_x outlet emission rates of 5 and 2 ppm at 5 ppm residual NH_3 will require annual testing and tuning to assure the requisite mixing of ammonia reagent and NO_x is achieved, likely to 5% RMS basis or less. This requirement will be particularly important for refinery applications, where fuel gas composition can significantly vary. The fixed cost of \$40,000 per year, per unit, will be added to these two design cases.

Discussions with refinery staff addressed the maintenance and administration requirements for existing SCR process equipment, but it did not provide any useful insight in assessing costs. Thus, the S&L-derived projections - amended to include annual testing to assure uniform reagent distribution and adopting owner-incurred fully burdened operator changes of \$100/hr - are adopted in the absence of any other information.

<u>Reagent Cost</u>. Reagent cost is straightforward to calculate. The most significant variable is the delivered cost of ammonia reagent to the site – and whether aqueous or anhydrous reagent is selected.

<u>Catalyst Replacement Costs</u>. These costs depend on the catalyst volume, which as described in Section 4.2, vary with volume estimated for achieving select NO_x outlet and residual NH₃ outlet values. The method for estimating catalyst volume should be revised to include the state-of-the-art understanding of process design. A revised procedure to estimate catalyst volume may not significantly affect estimated capital cost, as discussed previously; a change in catalyst volume could affect a capital estimate by 5-10%, well within the accepted accuracy of the EPA cost estimating procedure. However, the revised catalyst volume will affect the variable operating cost for catalyst management, which could be a significant consideration when targeting very low NO_x levels.

Table 4-2 shows the annualized catalyst replacement cost for achieving 7, 5, and 2 ppm outlet NO_x starting with a 40 ppm inlet concentration, based on the volume of catalyst calculated in Table 4-1. The values in Table 4-2 are derived from the catalyst estimated in Table 4-1, with the total inventory annualized over the five year period, using the total catalyst delivery and removal/installation charge of \$12,500 per m³ of catalyst. Table 4-2 shows that the annualized cost to achieve the lowest NO_x level is 60% greater than the projected cost by the EPA procedure.

Table 4-2.	Annualized Catalyst Replacement Cost to Achieve Three NO _x Limits: EPA vs
	Catalyst Suppliers Estimates ¹

Inlet NOx (ppm,	Outlet NOx (ppm,	Annual Cost, EPA	Annual Cost,
at 5% O2	at 5% O2)	(\$/y)	Supplier RP (\$/y)
40	7	30,188	30,913
40	5	36,226	42,259
40	2	51,320	80,159

¹ Catalyst replacement cost of \$10,000/m³, with an additional 25% charge for removal and installation.

<u>Auxiliary Power</u>. The auxiliary power cost is determined by the entire SCR process, mostly flue gas pressure drop but also operation of reagent supply equipment, and the unit price of power charged. The wholesale power price assumed for the Los Angeles metropolitan area is \$120/MWh.

In summary, the SCR Cost model can be used to estimate incurred NO_x control cost to the accuracy of a conceptual study, and deliver estimates that could be 30% below or 50% above the value achieved with 80% confidence. This approximation is in contract to a detailed "Class 1" engineering study (i.e., $\pm 10-15\%$). The SCR Cost Model as presently maintained by South Coast AQMD features updated capital cost relationships, based on recent estimates determined by the refineries and submitted through the WSPS. Fixed O&M costs use the method adopted from the S&L source study and are augmented with annual costs for tuning of reagent AIG. The method for estimating catalyst volume could be altered to reflect state-of-art understanding and assure that correct variable operating cost reflect units operating at very low NO_x levels.

The SCR Cost Model, with these modifications, can be used to provide budgetary costs to assess trends. A more robust approach to estimate cost is to use refinery-owner detailed engineering, combined with the catalyst volume estimating procedure developed by catalyst suppliers.

SITE VISIT OBSERVATIONS

Site visits comprising a team of FERCo and South Coast AQMD staff were made to five Southern California refineries. The purpose of the site visits was to discuss the refineries plans and issues with respect to Proposed Rule 1109.1 and to physically observe the challenges the refineries would face in implementing BARCT on their equipment.

5.1 New BARCT SCR Systems

All of the sites visited said that without knowing the BARCT limits and the equipment affected only preliminary planning could be done. They reviewed their current on-going work for the NO_x shave program. While a number of the units involved in the NO_x shave program will use SCR, either in design, or being implemented, the design target for exit NO_x is not as stringent as the expected BARCT limit (e.g., 2, 5, 7 or 9 ppm). In addition, since the NO_x shave program only affected a limited number of devices, the refiners could select the easiest systems to retrofit. During the site visits, refiners pointed out the devices where they felt SCR could not be retrofit. Yet, for the NO_x shave program, they also showed on-going or planned SCR projects employing some clever approaches for SCR implementation. For instance, for a couple of devices, air preheaters will be removed to accommodate the SCR reactor. For another unit, an abandoned ESP will be partially dismantled but the main steel structure will remain in place to support the new SCR reactor. Yet, in another source the flue gas from two heaters will be ducted across a road to the SCR reactors built on available open space. Until BARCT limits are established and refineries and their associated engineering companies can seriously look into retrofits, it is difficult to say what fraction of the units may not be candidates for SCR retrofits.

5.2 Existing SCR Systems

There is a fair number of SCR systems on refinery equipment that were installed during the RECLAIM Program. These units typically did not have a NO_x limit and the NH₃ limit is likely 20 ppm given the time period that they were installed. As discussed in Section 2, as the NO_x reduction that the SCR needs to attain increases, so does the amount of catalyst, and the NH₃/NO_x ratio entering the catalyst needs to improve. From the site visits it was observed that 1) the ammonia injection grid (AIG) designs were quite simple 2) in some cases there were no sample ports at the exit of the SCR catalyst that would be used to "tune" the AIG. The refinery owners will need to assess each of these existing SCR units to determine what modifications will need to be done to meet the BARCT limit. These modifications will include but not necessarily be limited to:

- Tune the AIG
- Replace and add additional SCR catalyst

- Replace the AIG
- Replace the SCR reactor and AIG

These modifications will need to be done on a unit-by-unit basis.

5.3 Suggested Improvements

During the site visits and during discussions with refinery personnel, we reviewed a number of planned SCR systems. Based on this review, there were a few suggested changes that can either reduce costs, improve performance, or both. Two examples are discussed below.

Cylindrical Heater

Figure 5-1 shows a typical arrangement for adding either an existing SCR or a planned SCR to a natural draft heater. In this arrangement, the flue gas is withdrawn from the base of the stack where it flows down to the SCR reactor and then goes through an induced draft fan which pushes the treated flue gas back to the stack. In this arrangement, the ammonia injection grid would be located in close proximity to the SCR catalyst. In fact, in most cases it will be incorporated into the SCR housing. Depending on the level of NO_x reduction that needs to be achieved, it may be difficult to achieve the necessary uniformity of the NH₃/NO_x ratio entering the catalyst with this arrangement.



Figure 5-1. Cylindrical Heater SCR Arrangement

There are two modifications that could be considered that can both reduce cost and likely improve performance. If aqueous ammonia is used as the SCR reagent, the reagent will be vaporized on the reagent skid, mixed with dilution air and then injected into the flue gas through a series of lances incorporated in the SCR housing.

This reagent system can be markedly simplified by just spraying the aqueous ammonia into the flue gas at the base of the stack, allowing it to vaporize as it flows down to the SCR reactor. A CFD or cold flow modeling study would determine if there is adequate mixing as it flows down to the reactor. Or, if a static mixer needs to be incorporated in the flow path. This approach is widely used in both industrial and large coal-based utility SCR systems.

This markedly simplified the reagent delivery system eliminating the vaporized/dilution air system which get replaced with a metering pump and dual fluid atomizer. This will also reduce the electrical consumption by the vaporizer.

A second modification that could be considered is to locate the fan upstream of the SCR reactor. With the fan located upstream of the SCR reactor, it will also function as a good ammonia/flue gas mixer assuming the aqueous ammonia is sprayed in as described above. The mixing across the fan would easily generate an NH₃/NO_x ratio with RMS less than 5%. This level of ammonia uniformly cannot be easily attained with the AIG located in close proximity to the catalyst, as shown in Figure 5-1.

5.4 Incinerator

During the visits we observed a number of incinerators that would also need to reduce NO_x . In these cases, the flue gas exiting the incinerator is at a temperature of up to 1800°F. One preliminary concept was to install a waste heat boiler to reduce the flue gas temperature with an SCR located downstream of the waste heat boiler. If the steam produced from the waste heat boiler is needed at the refinery, then this approach makes sense. However, if the cost of the waste heat boiler is considered part of the NO_x reduction system, the NO_x reduction costs in terms of \$/ton will be extremely high.

An alternate approach would be to adopt an arrangement that is commonly used on simple cycle such as turbine SCR systems. In these systems, the flue gas exiting the gas turbine can reach a temperature of $1000 - 1150^{\circ}$ F. A fan is used to dilute the flue gas with "tempering air" to a temperature of $800 - 850^{\circ}$ F before entering the SCR catalyst. This approach should be substantially less costly than utilizing a waste heat boiler. The overall flue gas flow rate through the SCR will increase which means the SCR reactor size will increase. But, the cost of a larger SCR reactor along with the tempering air fans is markedly less than the waste heat boiler approach.

5.5 Dual SCR Reactors in Series

The implementation of SCR NO_x control on refinery heater systems can be challenging for many reasons. First and foremost, the physical spaces around these heater units are typically very congested. These space constraints can significantly limit the distance available between the AIG and the SCR catalyst itself. As discussed previously, achieving very high levels of SCR NO_x removal (90% to 98%) requires exceptionally good mixing of the ammonia into the flue gas stream ahead of the catalyst. RMS NH_3/NO_x mixing levels of less than 10%, and sometimes

down to 5%, will be necessary to achieve NO_x removals in excess of 95%. During the site visits, the hosts pointed out refinery units where they felt space was too limited to retrofit an adequate SCR system. In these cases, one alternative that may be feasible would be to split the SCR catalyst volume between two reactors in series (each housing to be equal to one-half of the total catalyst volume) where additional mixing of the flue gas stream could be accomplished between the two reactors. In this arrangement, all the ammonia would be injected through the AIG upstream of the first reactor, and the mixing between the reactors accomplished by placing a simple bluff-body mixing device in the duct connecting the two reactors. The connecting duct would need to be of a cross-sectional area smaller than the reactors in order to increase the flue gas velocity and maximize the efficiency of the mixing device. This approach will increase pressure drop across the SCR system and may require a larger fan.

The tables below provide the results of example calculations performed by FERCo, utilizing their proprietary, in-house SCR process model. The example calculations are based on unit data for a heater, as well as SCR catalyst activity and deactivation rate data typical for refinery heater applications. Assuming an inlet NO_x level of 70 ppm_c, and outlet NO_x and ammonia slip permit requirements of 2 ppm_c and 5 ppm_c, respectively, the required NO_x reduction level is 97.1%. End-of-life (EOL) calculations are assumed to be 40,000 hours or 4.6 years. Table 5-1 shows the calculation results assuming a very good NH₃/NO_x distribution (RMS = 5%) into the catalyst. In this case, a total catalyst volume of 10.2 m³ is required. When the catalyst is new (K/Ko = 1.0), the outlet NO_x and slip levels are well below the permit requirements at 0.76 ppm_c and 3.76 ppm_c, respectively. At EOL (K/Ko = 0.7), the catalyst activity has degraded and both the outlet NO_x and slip levels have increased to just below the permit limits at 1.98 ppm_c and 4.98 ppm_c, respectively.

	Single Reactor	Single Reactor
	new	EOL
K/Ko	1.00	0.70
NOx-in, ppm	70.00	70.00
NOx-out, ppm	0.76	1.98
dNOx, %	98.9	97.2
NH3 slip, ppm	3.76	4.98
NH3/NOx-in	1.043	1.043
RMS-in, %	5.00	5.00
NH3/NOx-out	8.39	2.48
RMS-out, %	74.76	64.31

Table 5-1. Example Calculations for SCR Retrofit to a Heater Inlet NH₃/NO_x RMS = 5%, and 10.2 m³ Catalyst Volume

In Table 5-2, we have assumed there is not sufficient distance between the AIG and SCR catalyst to get the NH_3/NO_x RMS down to 5%, but an RMS of only 15% is achievable. Assuming the same volume of catalyst in the example above (10.2 m^3) , the Single Reactor columns in Table 5-2 indicate the NO_x and ammonia slip permit requirements of 2 ppm_c and 5 ppm_c, respectively, are not met even when the catalyst is new (K/Ko = 1.0). However, if the catalyst volume is split between the two reactors in series (each housing 50% of the total catalyst volume), and we introduce some mixing in between the reactors, the Split Reactor columns in Table 2 show the permit requirements can be met without adding any additional catalyst. The NH_3/NO_x RMS level leaving the first reactor is 63.1%, and mixing the flue gas between the two reactors to reduce the RMS level into the second reactor to 15% results in a significant increase in overall SCR system performance.

	Single Reactor	Single Reactor	or Two Split Reactors, WITH mix	
	new	EOL	Reactor 1	Reactor 2
K/Ko	1.00	0.70	0.70	0.70
NOx-in, ppm	70.00	70.00	70.00	12.73
NOx-out, ppm	3.54	4.56	12.73	1.95
dNOx, %	94.9	93.5	81.8	84.7
NH3 slip, ppm	6.54	7.56	15.73	4.98
NH3/NOx-in	1.043	1.043	1.043	1.238
RMS-in, %	15.00	15.00	15.00	15.00
NH3/NOx-out	12.85	3.36	1.24	2.37
RMS-out, %	105.24	101.88	63.10	43.07

Table 5-2. Example Calculations for Heater SCR Performance with Inlet NH₃/NO_x RMS = 15%, and 10.2 m³ Catalyst Volume

Simply increasing the catalyst volume is an approach often suggested to compensate for poor NH₃/NO_x mixing ahead of the reactor. While this approach sometimes works in applications where lower overall NO_x removals are required, it does not work at the high NO_x removal levels required for the applications discussed herein. Table 5-3 below shows the Single Reactor calculations run in Table 5-2 above (NH₃/NO_x RMS = 15%), but with three times the catalyst in the reactor (30.6 m³). While there is a moderate improvement in the EOL outlet NO_x and ammonia slip levels, neither value is below the allowable permit levels of 2 ppm_c and 5 ppm_c, respectively.

	Single Reactor	Single Reactor	
	new	EOL	
K/Ko	1.00	0.70	
NOx-in, ppm	70.00	70.00	
NOx-out, ppm	3.28	3.28	
dNOx, %	95.3	95.3	
NH3 slip, ppm	6.28	6.28	
NH3/NOx-in	1.043	1.043	
RMS-in, %	15.00	15.00	
NH3/NOx-out	0.00	0.00	
RMS-out, %	613.54	609.27	

Table 5-3. Example Calculations for Heater SCR Performance with Inlet NH_3/NO_x RMS = 15%, and 30.6 m³ Catalyst Volume

Tables 5-1 and 5-2 above demonstrate that EOL values of 2 ppm_c NO_x and 5 ppm_c ammonia slip can be achieved with the same volume of catalyst (10.2 m³) under two distinctly different inlet NH₃/NO_x RMS conditions. With 5% inlet RMS the total catalyst volume can be placed in a

single reactor. However, at 15% RMS the total catalyst volume has to be split between two reactors in series and the mixing stage introduced ahead of the second reactor. While there will be cost associated with splitting a single reactor into two smaller ones, and additional ductwork and flue gas mixing between the two reactors, this is an approach to be considered in cases where very high levels of NO_x removal are required, but exceptionally good mixing of the ammonia into the flue gas stream ahead of the catalyst (NH₃/NO_x RMS = 5%) is not achievable.

5.6 Major Modification to an Existing SCR

In some cases, a major modification may be necessary to an existing SCR in order to meet the BARCT limit. This is the case for an LM6000 gas turbine operated by Burbank Power and Light. The existing design of the unit was barely able to meet a 5 ppm NO_x /5 ppm NH₃ slip limit. A major modification is necessary to meet the SCAQMD 1135.1 NO_x limit of 2.5 ppm with a 5 ppm NH₃ slip limit. Figure 5-2 shows the existing configuration of the SCR/CO catalyst system on the unit. Noteworthy is that the AIG, located downstream of the CO catalyst, has no adjustment valves. In 2010 this unit could not comply with the 5 ppm NO_x and 5 ppm NH₃ slip limits. Testing to characterize the NH₃/NO_x distribution ratio entering the SCR catalyst yielded an RMS of 31%. This was traced in the injection holes in the AIG resulting in more ammonia being injected at the top and bottom of the reactor and to one side (Figure 5-3). Resizing the holes reduced the RMS to 15.5% and then selectively modifying holes resulted in a further reduction in the RMS to 12.5%. This is not adequate to meet the 2.5 ppm NO_x limit.

The suggested modification is shown in Figure 5-4. This involves:

- Removing the CO catalyst
- Removing the AIG
- Replacing the existing SCR catalyst with a new dual function SCR/CO catalyst available from major catalyst suppliers
- Relocating the AIG to the flow channels defined by the vanes near the entrance to the SCR box where better mixing of the reagent with the flue gas will occur

Physical cold flow modeling indicates that an NH_3/NO_x RMS of 2% is expected from this modification (Figure 5-5). This is an extremely low RMS for a gas turbine SCR system. This unit has a flue gas flow rate of nominally 1,000,000 lb/hr. A preliminary cost estimate for this retrofit is about 1.4 million dollars, \$500,000 being the cost of the dual function catalyst. The heat input of this gas turbine is on the order of 400MMBtu/hr.

Again, this illustrates the type of modifications that may be necessary to existing SCR systems to meet BARCT limits.







Figure 5-3. NH₃/NO_x Ratio As-found and With Modified AIG Holes



Figure 5-4. Recommended Modifications to existing SCR



Figure 5-5. Physical Cold Flow Model NH₃/NO_x (Tracer Gas) Distribution

5.7 Fluid Catalytic Cracker (FCC) Units

During one of the site visits an FCC unit was inspected that was equipped with two (2) Electrostatic Precipitators (ESPs) to remove particulate from the flue gas. The original ESP is still in use along with a second ESP with higher specific collecting area (SCA) and thus higher particulate matter removal efficiency. The owner stated that the second ESP was installed to augment control of fine particles. The ESP units are arranged in a series, with the original ESP upstream of the newer ESP.

The owner stated that limited space in the immediate vicinity of the FCC prevents a conventional SCR from being installed. Also in close proximity to where the SCR would be installed are emergency flares that are used to burn hydrocarbons that need to be vented in the event of equipment malfunction. The flare discharge appears to be within 100 meters of the location where the SCR would be installed, potentially endangering labor crews if activated during the construction process.

South Coast AQMD data lists the FCC unit gas flow rate at about 86,000 scfm.

One option for this site is to convert the original ESP – still energized and providing particulate removal - to a hot gas filtration system with ceramic-based filters that incorporate SCR capability (Ultra Cat). This option would transfer the majority of the particulate removal operations to the initial ESP chamber – now converted to a ceramic filter – while enabling NO_x reduction within the same chamber. Similar catalytic filters are widely used in the glass industry, where they are subject to high particulate loads similar to those in an FCC unit. This hot gas filtration system operates without water. Figure 5-6 shows a schematic of such system.



Figure 5-6. Catalytic Hot Gas Filtration System

The catalytic filter elements are coated on the inside with the same active ingredients used for conventional SCR catalyst – a combination of vanadium pentoxide (V2O5) and tungsten oxide

(WO3). The ancillary SCR equipment is identical to conventional SCR – equipment for reagent storage, transport, injection, and distribution within the gas stream.

The process equipment supplier reports that these systems are capable of NO_x reductions greater than 90%.

The unique features of this site enable installation of the catalytic filter process without imposing significant equipment downtime. To enable refinery operation during installation, a flue gas bypass duct would be installed to direct all product gas to the second, newer ESP – which with enlarged SCA is capable of handling the full FCC particulate loading. The initial ESP then "de-activated" can be converted to the catalytic filter while the FCC continues to operate.

Based on Google Earth views, the two original ESP boxes are nominally 24 feet by 40 feet, see Figure 5-7. The two boxes provide a surface area of about 1920 square feet, allowing for up to 2400 filter holes. Using 4 meter catalytic filter elements would provide a capacity of 96,000 scfm, or about 15 percent margin.

Based on experience with the glass industry, the process supplier estimates an installed cost for the catalytic filtration process as retrofit into the initial ESP cavity as approximately \$10M. However, this estimate does not include the installation of the gas bypass duct and the modification of process controls to continue FCC operation during the construction process. The estimate also does not account for workforce productivity in a refinery environment, which due to high safety standards is typically lower than observed productivity in other industries. Thus, the \$10 M estimate would have to be adjusted to account for these factors, and can be expected to escalate by an unknown amount which could be significant.



Figure 5-7. Two ESPs in Series on an FCC Unit

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CONCLUSIONS

Based on the work conducted during this study along with the information gathered during site visits to five (5) refineries, the following conclusions can be made:

- 1. Refineries may be space-challenged to install SCR on some devices.
- 2. Some clever engineering is taking place for some SCR systems being installed as part of the NO_x shave.
- 3. Based on the site visits and discussions with refinery staff, there are some approaches worthy of consideration to enhance SCR performance and/or reduce cost:
 - > Heaters direct injection of aqueous ammonia
 - > Heaters utilize a booster fan as an ammonia mixer
 - FCC Unit consider retrofitting one of two ESPs arranged in series with catalytic filters widely used in the glass industry
 - Incinerators consider using tempering air to reduce gas temperature as is widely done with simple cycle gas turbines
- 4. Further lowering NO_x emissions could increase those of particulate matter, thus refinery gas sulfur content and the resulting particulate formation due to reaction with SCR NH₃ slip needs consideration.
- 5. To achieve the maximum emission reductions, a combination of LNB/ULNB and SCR will be necessary for devices with high NO_x emissions.
- 6. The EPA NO_x costing model could be improved to better reflect refinery SCR systems, most notably the methodology to estimate the required catalyst volumes based on the current catalyst technology that is available.
- 7. Existing refinery SCR systems will need to be evaluated on a case-by-case basis to see how they can be upgraded to meet the new BARCT limit, or if major modifications are necessary.