TECHNICAL EVALUATION
AND
PRELIMINARY DETERMINATION

Florida Rock Industries, Inc.
Thompson S. Baker Cement Plant

Portland Cement Manufacturing Facility

Selective Non-Catalytic Reduction Installation on Kiln 1

Alachua County

DEP File No. 0010087-021-AC

Florida Department of Environmental Protection
Division of Air Resource Management
Bureau of Air Regulation

September 14, 2006

TECHNICAL EVALUATION AND PRELIMINARY DETERMINATION

I. APPLICATION INFORMATION

APPLICANT NAME AND ADDRESS

Florida Rock Industries, Inc
4000 NW CR 235
Newberry, Florida 32669
Authorized Representative: Chris Horner, Plant Manager

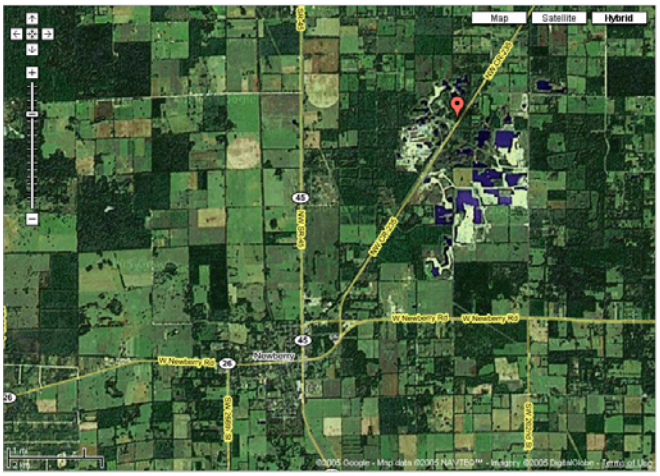
PROCESSING SCHEDULE

- Received Air Construction Permit Application on May 24, 2006
- Received letter waiving 90 day permit processing clock on August 14, 2006
- Intent to Issue Air Construction Permit distributed September 13, 2006

FACILITY DESCRIPTION AND LOCATION

Florida Rock Industries, Inc. (FRI) owns and operates the Thompson S. Baker Cement Plant on Alachua County Road 235, 2.5 miles northeast of Newberry, Alachua County. The plant has a current capacity of 2,650 tons of clinker per day on Kiln 1. A second kiln was approved in June 2005. The location of the Thompson S. Baker Cement Plant is shown in the figures below. The UTM coordinates of the Florida Rock facility are Zone 17, 346.8 km East and 3287.0 km North.

Figure 1. Location of Newberry



Location of Thompson S. Baker Cement Plant

FACILITY CLASSIFICATION CODE (SIC)

Major Group No. 32, Clay, Glass, and Concrete Products
Industry Group No. 324 Cement, Hydraulic
Industry No. 3241 Cement, Hydraulic

REGULATORY CATEGORIES

The following regulatory classifications apply to the subject facility:

Title I, Section 111, Clean Air Act (CAA): This facility is subject to certain Standards of Performance for New Stationary Sources. They are adopted and incorporated by reference in Rule 62-204.800, F.A.C. These inlcude:

- 40 CFR 60, Subpart A - General Provisions.
- 40 CFR 60, Subpart F - Standards of Performance for Portland Cement Plants. Certain requirements from Subpart F are replaced by requirements from 40 CFR 63, Subpart LLL listed below.
- 40 CFR 60, Subpart Y - Standards of Performance for Coal Preparation Plants.
- 40 CFR 60, Subpart OOO - New Source Performance Standards For Nonmetallic Mineral Processing Plants.

Title I, Section 112 CAA: The facility has the potential to emit 10 tons per year or more of any one hazardous air pollutant (HAP) or 25 tons per year or more of any combination of HAPs. This facility is subject to the Major Source provisions of:

- 40 CFR 63 Subparts A - National Emission Standards for Hazardous Air Pollutants – General Provisions.
- 40 CFR, Subpart LLL - National Emission Standards for Hazardous Air Pollutants from the Portland Cement Manufacturing Industry.

Title I, Part C (PSD): The facility is located in an area designated as "attainment", "maintenance", or "unclassifiable" for each pollutant subject to a National Ambient Air Quality Standard. The facility is considered a "portland cement plant", which is one of the 28 Prevention of Significant Deterioration (PSD) source categories with the lower PSD applicability threshold of 100 tons per year. Potential emissions of at least one regulated pollutant exceed 100 tons per year. Therefore, the facility is classified as a PSD-major source of air pollution with respect to Rule 62-212.400, F.A.C., Prevention of Significant Deterioration.

Title IV, CAA: The facility does not operate any units subject to the Acid Rain provisions of the Clean Air Act.

Title V, CAA: The facility is a Title V or "Major Source" of air pollution because the potential emissions of at least one regulated pollutant exceed 100 tons per year or because it is a major source of HAPS. Regulated pollutants include pollutants such as carbon monoxide (CO), nitrogen oxides (NO_X), particulate matter (PM/PM_{10}), sulfur dioxide (SO_2), and volatile organic compounds (VOC).

II. EXISTING FACILITY

The Florida Department of Environmental Protection ("Department") issued a permit to FRI in December 1996 to construct a Portland cement plant. The plant employs the modern dry process technology including a preheater and calciner along with indirect firing. The dry process preheater/calciner (PH/C) kiln is the most fuel-efficient cement pyroprocessing technology currently in use in the United States.

FRI completed construction of the basic plant in late Fall of 1999. The permit was modified in 2001 and 2002 to incorporate the final NO_X control plan, a VOC continuous emission monitoring system (CEMS), final emission limits and final production limits. The plant is presently permitted to make 2650 tons per day (TPD) of clinker with an hourly production rate of 110.2 TPH (115 TPH peak) and an annual production limit of 800,000 TPY.

The major equipment at the plant includes the PH/C kiln, a clinker cooler, raw mill, finish mill, silos, conveyers, and particulate control/dust collection and recycling equipment. The cement product is stored in silos and is shipped in bags or in bulk by rail or truck.

The following Figure is of a PH/C kiln that, with the exception of the calciner, approximates the one installed at FRI. The calciner arrangement at Florida Rock is shown separately as a diagram within the large diagram. Tires (mechanism not shown) are also introduced at the kiln inlet.

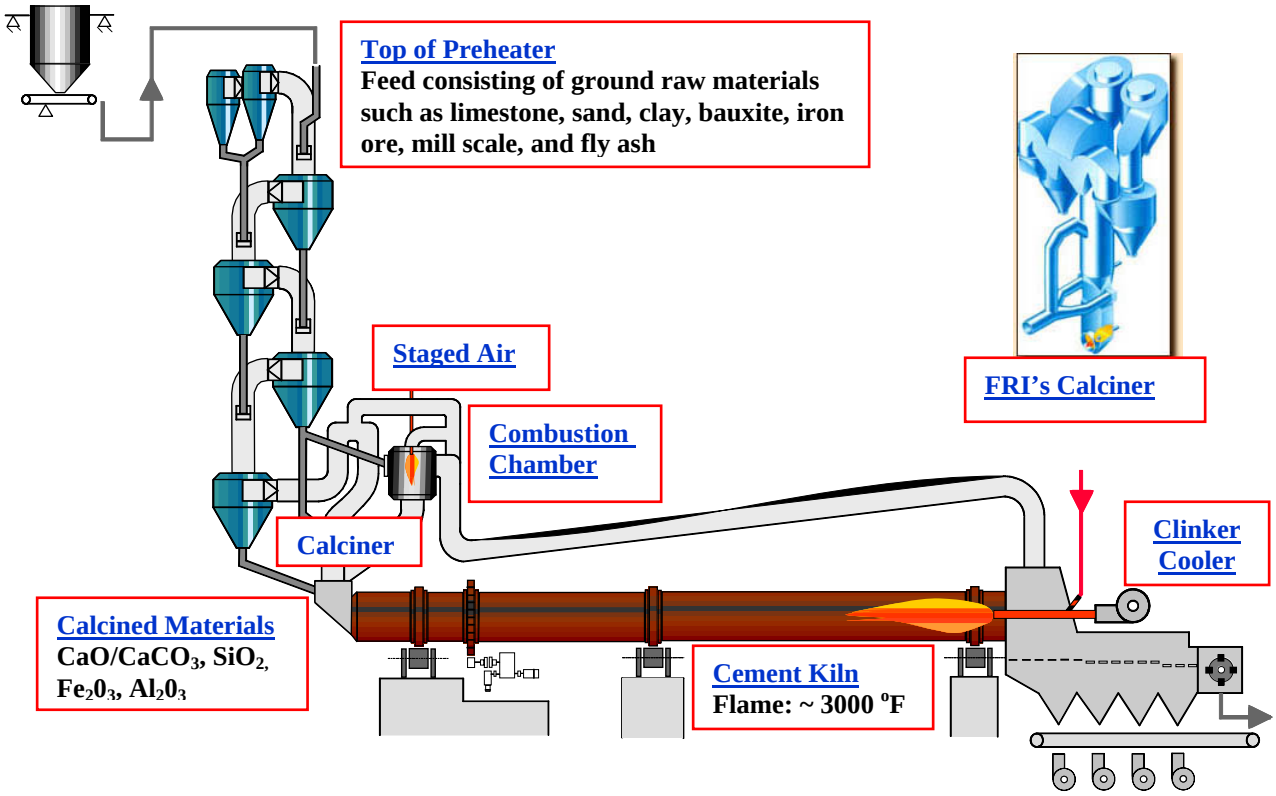


Figure 2. Diagram of Dry Process Cement Kiln with Preheater and Staged Air Calciner

Raw meal is finely divided dried material that includes sources of calcium, silica, iron and aluminum. These sources can include limestone, sand, clay, bauxite, iron ore, mill scale, and fly ash. It is continuously weighed on feed scales and introduced at the top of the preheater tower as shown in the diagram. As it falls through the preheater it is contacted and progressively heated by exhaust gases from the calciner and kiln.

The calciner has a separate horizontally mounted burner that provides the necessary heat to drive off carbon dioxide from the limestone converting it to free lime ($CaCO_3 = CaO + CO_2$). The calciner operates at a temperature in the range of 900 to 1000 degrees Celsius (°C) and burns coal. Tires are burned near the kiln inlet and reduce the load on the kiln and calciner burners.

The calcined materials enter the kiln where they are further heated and transformed into nodules of clinker. These exit the kiln near the main kiln coal burner that operates at the temperature necessary to make good clinker. This could be on the order of approximately 1,650 °C. The clinker falls into the cooler where it is cooled by ambient air.

The heated air from the clinker cooler is used as secondary air to support combustion at the kiln burner and is also conveyed along a tertiary air duct to support combustion in the calciner.

Cooled exhaust gases leaving the preheater go through the raw mill (not shown) where the remaining heat is used to dry incoming coarse raw materials. As the raw materials are ground they are lifted by the exhaust gas flow and conveyed to the main electrostatic precipitator (ESP - not shown) that also serves the purpose of a particulate control device. The finely divided dry material in the baghouse is conveyed to storage silos and then weighed and introduced into the process at the top of the preheater as discussed above.

Following is a photograph of the constructed plant taken in 2001.

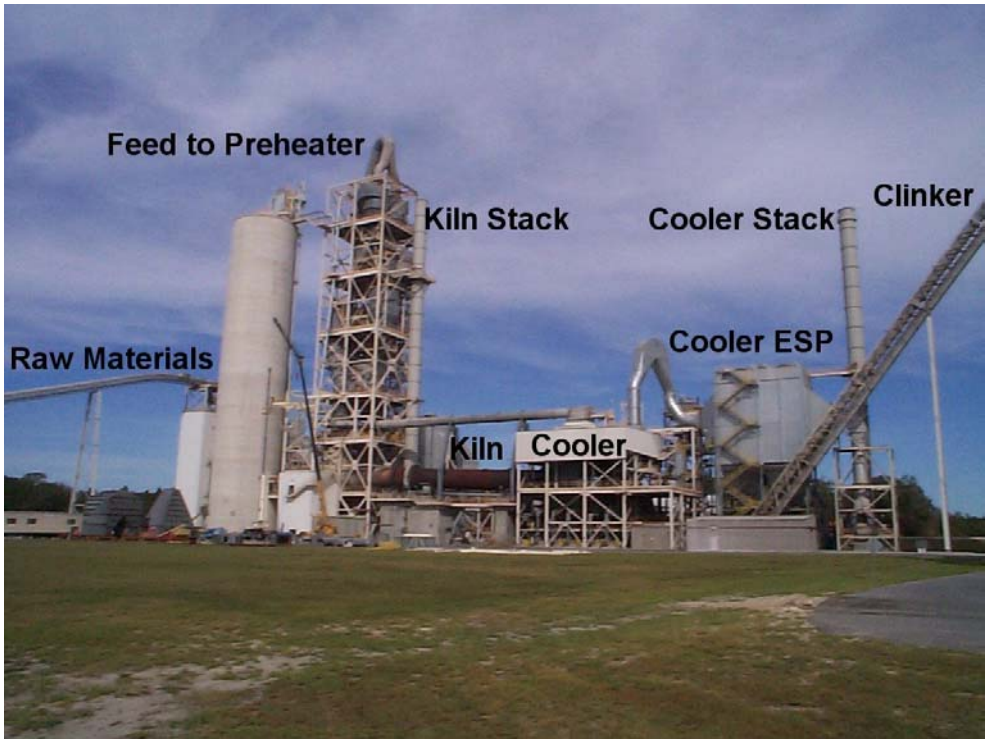


Figure 3. Florida Rock Industries' Cement Plant in Newberry, Florida

III. Application Proposal

FRI requested an air construction permit to install a Selective Non-Catalytic Reduction (SNCR) system on Kiln 1 as a means to provide greater control in kiln NO_X formation and emissions and flexibility in kiln operating parameters. The process utilizes injection of ammonia near the lowest preheater cyclone. The equipment consists of a storage tank, piping, pumps, compressed air and one or more injectors.

The following diagram illustrates the typical equipment needed for permanent ammonia (NH_3) solution storage and piping at a power plant. The cement plant requirements are similar. Initially, FRI will use tanker trucks for storage.

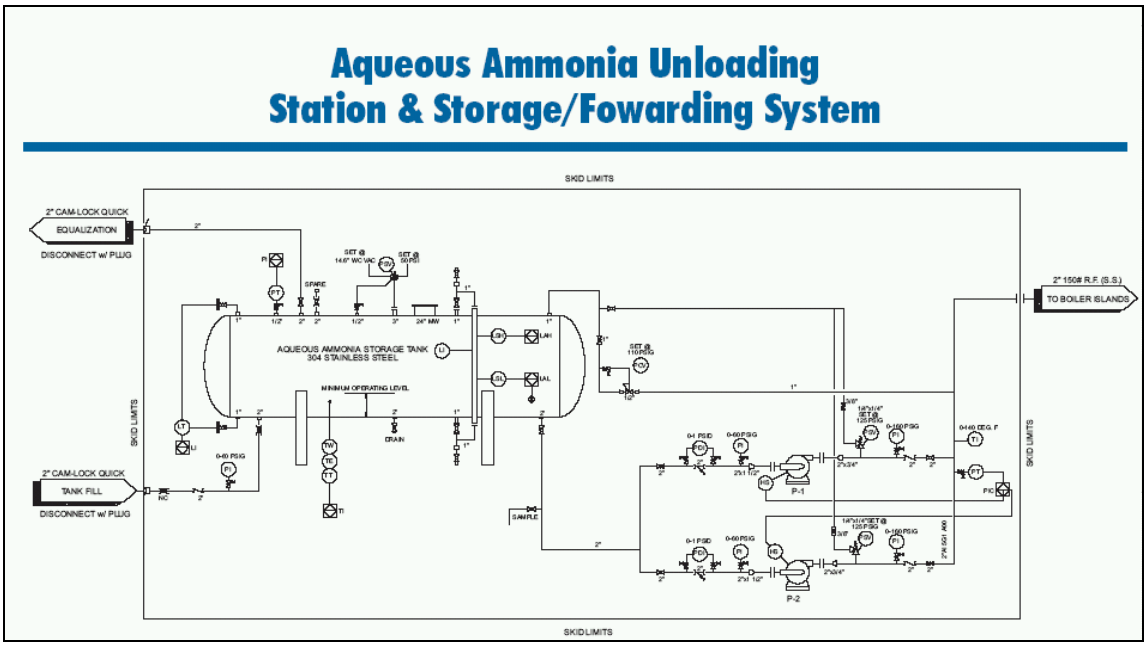


Figure 4. Diagram of Typical SNCR Ammonia Storage and Piping/Pumping System

No increases in previously-permitted production rates or emissions limitations are requested with this application.

IV. Selective Non-Catalytic Reduction Project

The selective non-catalytic reduction (SNCR) project is for the purpose of providing greater control in kiln NOx formation and emissions as well as flexibility in kiln operating parameters. The system is an alternate control strategy for meeting the applicable BACT determination made by the Department in December 2002.

Although there is a lot of recent experience with application of SNCR to cement plants in Europe, there is little experience with this technology at cement plants in the United States. Since March 2005, the nearby Suwannee American Cement has operated using SNCR, adhering to permitted emissions with regards to NOx and Ammonia slip. Prior to reviewing the technology, it is useful to describe the original NO_X control strategy at FRI.

Present Staged Combustion NO_X Technology at FRI

Florida Rock has a staged air and fuel calciner as shown in the small diagram within previous Figure 2 on Page 4. The calciner burner is horizontally mounted approximately halfway up the calciner vessel. Instead of using a kiln inlet burner as shown in the diagram, FRI introduces tires at the kiln inlet.

The principle of operation of staged combustion calciner at FRI is as follows:

NO_X-containing exhaust gas leaving the kiln is characterized by excess air and high temperature that is less than required to sinter cement but greater than required to calcine raw meal.

Equation 1. Calcination of limestone occurs at approximately 900 degrees Celsius (°C) and liberates carbon dioxide to produce lime according to the following endothermic reaction:

$$CaCO_3 \rightarrow CaO + CO_2$$

This reaction tends to rapidly cool the kiln exhaust gas. The additional heat supplied by the calciner burner and tires and tertiary air sustains the reaction. This tends to limit the temperature of exhaust gases in and leaving the calciner to temperatures less than 900 °C. Combustion in the calciner proceeds as follows.

Equation 2. Fuel, such as a volatile coal, is heated and pyrolyzed releasing hydrocarbon radicals. These, in turn, *catalytically* react with NO to form hydrogen cyanide according to:

$$CHi^* + NO \rightarrow HCN + ...$$

Where:

i = 1, 2, 3

Equation 3. Ammonia-like radicals are also released during pyrolysis and, under reducing conditions in the presence of raw meal, destroy NO according to:

$$NHi^* + NO \rightarrow N_2 + ...$$

This reaction suppresses formation of NO by the pyrolyzed fuel nitrogen and reduces NO_X in a manner that looks similar to the mechanisms of SNCR and SCR.

Other reactions involving carbon monoxide (CO) or hydrogen (H_2) are also *catalytically* driven and destroy NO_X in a reducing atmosphere. In the subsequent burning of soot and char, the NO_X reducing reactions proceed much more slowly and some of the remaining fuel nitrogen can form additional NO_X.

This technique (staged fuel and air combustion in the calciner) is used to meet the requirements of the December 2002 BACT determination.

Mechanisms of Selective Non-Catalytic Reduction (SNCR)

NH_3 in the form of ammonia water or urea is injected at a point in the process characterized by a suitable temperature window between 850 and 1050 °C depending on residence time, turbulence, oxygen content, and a number of other factors specific to the given gas stream. SNCR destroys NO_X by a two-step process as follows:

Equation 4. Ammonia reacts with available hydroxyl radicals to form amine radicals and water per the following theoretical equation:

$$NH_3 + OH^* \rightarrow NH_2{}^* + H_2O$$

Equation 5. Amine radicals combine with nitrogen oxides to form nitrogen and water.

$$NH_2{}^* + NO \rightarrow N_2 + H_2O$$

Equation 6. The two steps are typically expressed as a single "global reaction".

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$$

The simplified equation does not convey the kinetics. But it suggests that, theoretically, SNCR will function best in an oxidizing atmosphere.

Equation 7. In a reducing atmosphere, CO competes with ammonia for available OH radicals

$$CO + OH^* \rightarrow CO_2 + H^*$$

Figure 5 shows that the necessary temperature window exists at least between the kiln inlet and the bottom cyclone that receives the exhaust from the calcination section. The physical extent of the window for oxidizing conditions depends on the damper positions for the tertiary air branches for the shown calciner design. In selecting a level (or levels) for ammonia injection there must be some optimization of temperature and oxygen.

Based on the foregoing, ammonia should be injected after introduction of tertiary air. There may also be favorable injection points closer to the kiln inlet if oxidizing conditions exist in the calciner. However if fuel nitrogen oxidation is not complete, then additional NO_X may be formed and avoid treatment by ammonia.

The following figure shows the range of temperature and oxidizing/reducing conditions prevalent in a calciner such as used at FRI. Theory and practice suggest that the best overall injection point should occur in the ductwork between the tubular section and the cyclones shown in the following diagram.

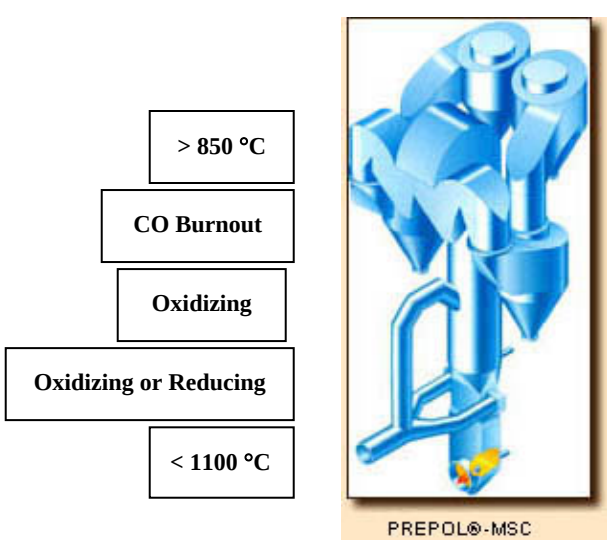


Figure 5. Temperature and Oxidizing Windows for SNCR in a Staged Combustion Calciner.

SNCR Testing at FRI

On November 8, 2004 the Florida Department of Environmental Protection (FDEP) issued Air Construction Permit 0010087-011-AC to FRI, authorizing tests to assess the viability of SNCR in controlling NO_X emissions produced in the main kiln. These tests were conducted during the period December 6-11, 2004.

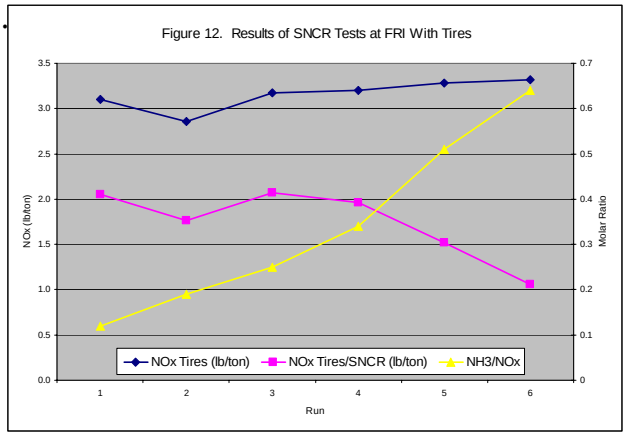
The Polysius Corporation designed the tests, supplied the equipment for the injection of ammonia, and provided personnel to operate the equipment. Additionally, Polysius monitored and reported the ammonia injection rates and the stack gas concentrations of NO_X and oxygen.

The following diagram shows some of the equipment and test points for a very similar test program conducted program also designed by Polysius at the nearby Suwannee American Cement Plant. Not shown is the metering system or the additional continuous emission monitoring equipment.

Figure 6. Aqueous Ammonia Supply Truck, Compressed Air, One of Four Ports, an Injector

At the FRI tests, plant personnel were responsible for operating the plant, reporting plant operating data and operating continuous emissions monitors for NO_X, SO_2, total hydrocarbons, and stack gas flow located in the kiln/raw mill stack. The consultant, Koogler & Associates, provided an engineer to oversee the tests and to monitor NH_3 and CO in the kiln/raw mill stack. The summary report is available at: www.dep.state.fl.us/Air/permitting/construction/flrock.htm

The Department reviewed the report and summarized the performance of the SNCR system in the graphs shown in the figure below. The graph on the left hand side represent the performance of the SNCR system while burning tires and maintaining mildly reducing or mildly oxidizing conditions in the calciner.



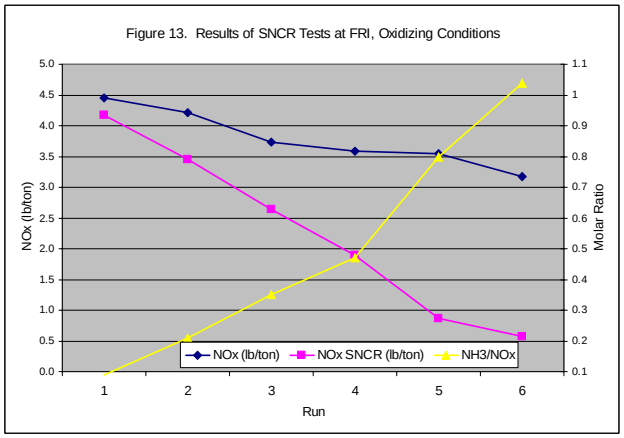


Figure 5. NO_X Emissions (middle lines) vs. Molar Ratio (lower lines) during Testing at FRI.

NO_X emissions prior to NH_3 injection are the values represented by the top (blue) line and range from 2.9 to 3.3 lb/ton clinker reference to the axis on the left. The middle (reddish) line represents NO_X emissions after injection of NH_3 at varying molar ratios (i.e. NH_3/NO_X). The bottom (yellow) line represents the molar ratio for the given trial. Emissions ranged from 1 to 2 lb/ton clinker for molar ratios between 0.65 and 0.11. The target emission limit of 2.45 can be met with minimal NH_3 usage. This is convenient because there should be very low NH_3 emissions (slip).

Separate tests were conducted for the case when no tires were combusted and the calciner was maintained in an oxidizing atmosphere. These are summarized in the graphs on the right hand side. NO_X emissions prior to NH_3 injection range from approximately 3.2 to 4.5 lb/ton clinker.

After NH_3 injection, emissions ranged from approximately 0.6 to 3.5 lb/ton clinker for molar ratios between 1 and 0.2. In this case, the target limit of 2.45 can be met at a molar ratio of approximately 0.4.

The key point is that the target emission rate can be met with relatively low NH_3 usage. This insures minimal CO increase or NH_3 slip. Any small CO increases will likely be offset by reductions caused by maintaining less aggressive reducing conditions (and possibly even oxidizing conditions) in the calciner.

The Department concludes that there is no reason to expect emission increases at the injection rates needed to comply with the present permit limits. The SNCR system is capable of reducing emissions to values less than the present tire introduction and staged combustion system. The SNCR can be used in conjunction with or in lieu of the present system to insure compliance with the permitted limit. It is an additional control strategy to the existing staged combustion system and will allow additional flexibility in achieving BACT.

V. APPLICABLE RULES

The Department has determined that the project is not a pollution control project to control one pollutant with collateral emission increases of other pollutants. Also it is not a pollution control project to control emissions where little or no controls presently exist. In fact at the present time the tire introduction and staged combustion in the calciner (with an aggressive reducing atmosphere) achieve good emission reductions to approximately 2 lb/ton of clinker. The SNCR system is expected to perform as well.

The Department does not expect actual emission increases of any pollutant, therefore the project is not a modification as described in 62-210.200 (Definitions). However a permit is still required in accordance with paragraph 62-210.300 that states:

"Unless exempted from permitting pursuant to paragraph 62-210.300(3)(a) or (b), F.A.C., or Rule 62-4.040, F.A.C., or unless specifically authorized by provision of Rule 62-210.300(4), F.A.C., or Rule 62-213.300, F.A.C., the owner or operator of any facility or emissions unit which emits or can reasonably be expected to emit any air pollutant shall obtain an appropriate permit from the Department prior to beginning construction, reconstruction pursuant to 40 CFR 60.15 or 63.2, modification, ***or the addition of pollution control equipment****; …… etc."*

VI. SPECIAL CONDITIONS FOR SNCR

Because SO_2 emissions are minimal from cement kilns in Florida, very little particulate matter can be formed by reaction with excess NH_3 emissions (slip). Although there is no reason to inject as much NH_3 as it takes to react with all NO_X, the Department will limit the maximum NH_3 injection rate to that level, at a molar ratio of 1.0. This equates to approximately 150 pounds per hour of ammonia (as 100% ammonia) assuming pretreatment emissions of 4 lb/ton of clinker. The actual delivered aqueous ammonia solutions will be in the range of 9 to 19 percent ammonia.

FRI will use the SNCR system at its option and is still required to retain the staged combustion calciner and the capability of operating the calciner in a reducing atmosphere in accordance with their previous construction permits and present Title V Operation Permit.

VII. ADDITIONAL COMMENTS

The Department's preliminary determination is based only on the facts presented by FRI and the Department rules sufficient to evaluate the proposed project.

Furthermore the Department's determination is strictly limited to this specific case and should not be used as a precedent for other cases, or lead to unintended consequences construed from the language contained in this determination. Ultimately, it is the Department that interprets its own regulations and opinions.