

Interim Report

***IN SITU* DEVICE FOR REAL-TIME
CATALYST DEACTIVATION MEASUREMENTS***

(DOE Project 42298)

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Abstract

SCR catalyst management has become an important operations and maintenance activity for coal-fired utility boilers in the United States. To facilitate this activity, a method to determine catalyst activity *in situ* is being developed. This report describes the methodology and presents the results of proof-of-concept tests conducted at Alabama Power Company's Gorgas Unit 10 during the 2005 ozone season. The proof-of-concept results showed that the *in situ* measurements are in agreement with the laboratory measurements and the technique has some advantages over the traditional laboratory method of determining catalyst activity. Continued testing and development is planned for the 2006 ozone season.

Acknowledgement

FERCo would like to acknowledge the co-sponsors of this program: NETL, EPRI and Southern Company. The input from Charles Miller (NETL), Keith Harrison (Southern Company), and Dave Broske (EPRI) have been key in making this project a success. We also thank Tara Harbin and the operating staff at Plant Gorgas for their efforts and cooperation, without which the work could not have been completed.

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1

INTRODUCTION

The U.S. utility industry, to date, has installed over 100 GW of selective catalytic NO_x reduction (SCR) systems on coal-fired utility boilers. In the SCR process, ammonia is injected ahead of a catalyst (primarily vanadia-titania based) where it reacts with NO_x, forming nitrogen (N₂) and water (H₂O). In coal-fired SCR systems the catalyst activity will gradually decrease over time, primarily due to the constituents in coal flyash. Furthermore, these coal-fired SCR systems contain multiple catalyst layers and each layer can exhibit a different rate of activity degradation. In addition to the decline in activity, with increasing operating hours the catalyst will become plugged with flyash, effectively reducing the active catalyst surface area. As the overall activity of the reactor decreases, a point will be reached where the system will no longer be able to achieve the designed level of NO_x reduction without increasing the ammonia flowrate. This will ultimately result in unreacted ammonia passing through the reactor (i.e., ammonia slip).

Ammonia slip can have detrimental downstream impacts. The ammonia can react with SO₃ in the air preheater resulting in ammonium bisulfate formation and air preheater pluggage. The ammonia can also become associated with the flyash to levels such that the flyash can no longer be sold. To avoid these impacts, ammonia slip is typically limited to 2 ppm.

As the catalyst activity degrades and ammonia slip increases, a point is reached where either additional catalyst must be added to the reactor, or some of the catalyst replaced with new material. To deal with these issues, utilities have undertaken catalyst management programs aimed at monitoring the activity of the SCR reactor. This typically involves experimentally monitoring the degradation in activity, as well as utilizing a software component to help plan when catalyst must be added, or replaced.

The current project is developing a new experimental approach to facilitate the determination of catalyst activity.

2

METHODOLOGY AND APPROACH

2.1 Catalyst Activity and SCR Reactor Potential

This subsection will discuss the various parameters that are important in determining the overall performance of an SCR system. In particular, the parameters that are of most importance are 1) catalyst activity, 2) reactor potential, and 3) area velocity.

To understand the importance of these parameters, consider a mathematical analysis of the processes that occur as the $\text{NH}_3\text{-NO}_x$ mixture flows through a catalyst passage. The following processes take place as the gas enters a catalyst channel:

1. The flue gas enters the catalyst channel with a concentration $\text{NO}_{x\text{in}}$
2. Before the NO_x can react with NH_3 on one of the "active" sites on the catalyst surface, it needs to migrate from the bulk gas to the surface of the catalyst. This is a mass transfer process that is described by equation 2-1 below. This mass transfer process occurs continuously along the length of the channel.

$$\left[\begin{array}{l} \text{Rate of NO}_x \\ \text{mass transfer} \\ \text{to the catalyst} \\ \text{surface} \end{array} \right] = h_m A_{\text{surface}} (C_{\text{NO}_x\text{gas}} - C_{\text{NO}_x\text{surface}}) \quad (2-1)$$

h_m = mass transfer coefficient
(depends on gas velocity and catalyst geometry)

A_{surface} = surface area of the catalyst channel

$C_{\text{NO}_x\text{gas}}$ = NO_x concentration in the gas phase

$C_{\text{NO}_x\text{surface}}$ = NO_x concentration on the surface

3. Once the NO_x reaches the surface of the catalyst, it will diffuse through the porous structure of the catalyst, and attach to an active site where it will react with NH_3 . The NH_3 will have gone through the same steps as the NO_x in terms of diffusing from the bulk

gas to the catalyst surface. The rate of reaction of the NO_x on the surface is described by equation 2-2 below.

$$\left[\begin{array}{l} \text{Reaction Rate} \\ \text{of NO}_x \text{ on the} \\ \text{surface} \end{array} \right] = -K_{\text{chem}} A_{\text{surface}} C_{\text{NO}_x \text{ surface}} \quad (2-2)$$

K_{chem} = chemical reaction rate constant that also accounts for pore diffusion

To solve these equations, it is assumed that the system is at steady state (i.e., at any place on the catalyst, conditions do not change with time). For this to be true, the rate of mass transfer to the surface must be equal to the rate of reaction; otherwise, the surface concentration would change with time. If equation 2-1 is set equal to equation 2-2, the surface concentration of NO_x may be calculated from:

$$C_{\text{NO}_x \text{ surface}} = \frac{1}{1 + \frac{K_{\text{chem}}}{h_m}} C_{\text{NO}_x \text{ gas}} \quad (2-3)$$

When these two relations (i.e., equations 2-1 and 2-2) are integrated along the entire length of the channel, the NO_x concentration exiting the channel can be calculated and thus the NO_x reduction determined. This results in the following relation for NO_x reduction

$$\Delta \text{NO}_x = 1 - e^{-\frac{1}{A_v} \left[\frac{1}{K_{\text{chem}}} + \frac{1}{h_m} \right]} \quad (2-4)$$

ΔNO_x = NO_x reduction expressed as a fraction
(or multiplied by 100 to be expressed as percent)

A_v = Area velocity, or flowrate through the channel
divided by surface the area of the channel

The term in brackets with K_{chem} and h_m is defined as the catalyst activity (K).

$$K = \frac{1}{\frac{1}{K_{\text{chem}}} + \frac{1}{h_m}}$$

$$\Delta \text{NO}_x = 1 - e^{-K/A_v} \quad (2-5)$$

The area velocity essentially defines the flue gas flowrate per unit catalyst surface area in the reactor:

$$A_v = \frac{Q}{A_{cat}} \quad A_v = \text{area velocity, m/hr} \quad (2-6)$$

$$= \frac{Q}{V_{cat} A_{sp}} \quad Q = \text{flue gas flowrate, m}^3/\text{hr at standard conditions} \quad (2-7)$$

A_{cat} = catalyst surface area, m²

V_{cat} = catalyst volume, m³

A_{sp} = catalyst specific surface area m²/m³

Note that the activity K, involves both the chemical activity on the surface of the catalyst and the mass transfer processes in the channel. Thus, the catalyst activity is not a fundamental property of the catalyst material, since geometry and velocity can influence the mass transfer coefficient (h_m). In particular,

- The same material fabricated with different channel openings can exhibit different activities.
- The same material and geometry with different flowrates (i.e., velocity) in the channel can exhibit different activities.

The overall reactivity of an SCR system is determined by a term referred to as the reactor potential (RP). The reactor potential is the catalyst activity multiplied by the total surface area of catalyst per unit of flue gas.

$$RP = \frac{K A_{sp} V_{cat}}{Q} = \frac{K}{A_v} \quad (2-8)$$

The reactor potential is a measure of the overall ability of the reactor to reduce NO_x. A certain level of reactor potential is needed to achieve a set NO_x reduction while limiting NH₃ slip to a specified level.

For an SCR reactor with multiple layers, the overall reactor potential is the sum of the reactor potential of each layer.

$$RP = \sum_{i \text{ layers}} RP_i = \sum_{i \text{ layers}} \frac{K_i}{A_{vi}} \quad (2-9)$$

Additionally, since some of the catalyst surface area for each layer will be lost due to plugging by flyash, equation 2-9 may be modified to account for this blockage.

$$\begin{aligned}
 RP &= \sum_{i \text{ layers}} \frac{K_i A_{\text{cat}_i}^{\text{clean}} (1 - B_i)}{Q} \\
 &= \sum_{i \text{ layers}} \frac{K_i (1 - B_i)}{A_{v_i}^{\text{clean}}}
 \end{aligned}
 \tag{2-10}$$

where, $A_{\text{cat}_i}^{\text{clean}}$ = Total surface area of the i^{th} layer without blockage

B_i = Fraction of the catalyst channels on the i^{th} layer that are blocked

$A_{v_i}^{\text{clean}}$ = Area velocity of the i^{th} layer without blockage

Equation 2-10 above provides a means to characterize the overall potential of an SCR reactor to remove NO_x . The reactor potential inherently accounts for both catalyst deactivation (K/K_0), as well as catalyst layer blockage, thereby providing a true assessment of the operating condition of the SCR reactor.

2.2 Laboratory Determination of Catalyst Activity and Reactor Potential

Traditionally, in order to determine the reactor potential, a utility will remove a sample of catalyst from each layer of the reactor. The samples are then sent out to a laboratory for an activity analysis. This is accomplished by placing the sample in a device that allows a flue gas stream (real or simulated) to be passed through the sample at temperature, NO_x , and flow conditions representative of those for the full-scale SCR reactor. Ammonia is injected ahead of the sample at a NH_3/NO_x ratio of 1.0 or 1.2, and the NO_x reduction across the sample is measured. The activity for the sample is then calculated by rearranging equation 2-5:

$$K = -A_v \ln (1 - \Delta\text{NO}_x) \tag{2-11}$$

Where A_v = the area velocity at which the test was conducted
(generally corresponding to the design area velocity)

ΔNO_x = the NO_x reduction measured in the laboratory
apparatus

Once the activity of each individual layer (K_i) is calculated using equation 2-11 above, all that is needed to determine the overall reactor potential from Equation 2-10 is an estimate of the blockage for each of the catalyst layers (B_i). Generally, this is accomplished by conducting a

visual inspection of the reactor, and this procedure will be discussed in more detail in Section 5. One important thing to note at this point in time however, is that when utilizing equation 2-10, the precision of the reactor potential calculation depends as much on the accuracy of the blockage estimate as it does on the determination of K.

2.3 *In situ* Determination of Reactor Potential and Catalyst Activity

Currently, most utilities operate their SCR systems only during the five-month ozone season. The seven-month non-operating season generally provides ample time to remove catalyst samples from the reactor, send them out for testing, receive the activity results, and if necessary, take corrective action by adding or replacing catalyst material prior to the next ozone season. However, this best-case scenario still only allows one data point per layer, per year. To comply with the upcoming Clean Air Implementation Rules, most utilities will be required to move to year-round operation of their SCR systems by 2009. This, combined with the trend of stretching the scheduling of major outages out to as far as 18 to 36 months, will result in far fewer opportunities to go inside the reactor to remove catalyst samples for activity analysis, as well as assess the blockage of the layers.

Fossil Energy Research Corp. (FERCo) has developed a new device (U.S. patent pending, patent application 20050255605) that allows the reactor potential and catalyst activity to be determined *in situ*. With this new approach to catalyst testing, the reactor potential and activity can be measured at any time, independent of unit outages. With multiple devices, each layer can be measured independently and a number of individual measurements can be made across a given catalyst layer.

Unlike the laboratory approach that measures the activity (K), and then uses the design area velocity (A_v) with an estimate of the blockage to calculate the reactor potential, this new device provides a direct measurement of reactor potential. The *in situ* measurement technique is similar to the laboratory measurement. A small auxiliary ammonia injection grid (AIG) is located above the section of catalyst to be tested. To make the measurement, ammonia is added such that the local NH_3/NO_x ratio exceeds 1.0, and the NO_x reduction across the test section is measured. This is illustrated in Figure 2-1 where these individual test modules are incorporated on each catalyst layer. Incorporating the expressions for reactor potential and catalyst activity in equations 2-9 and 2-11 above yields the following expression, which indicates that reactor potential can be directly determined by measuring the NO_x removal across the *in situ* test module.

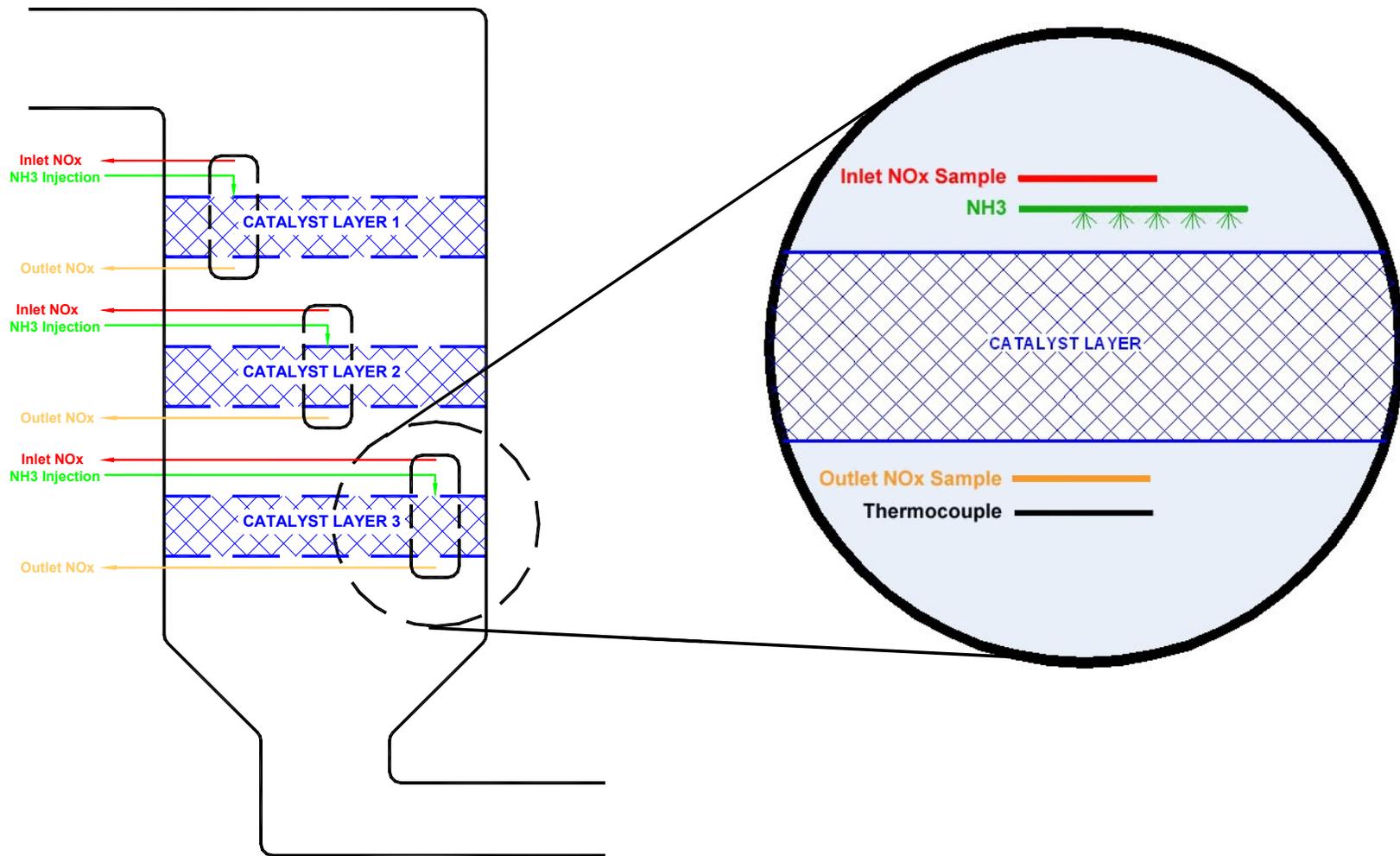


Figure 2-1. *In situ* Determination of SCR Reactor Potential

$$RP_i = \ln (1 - \Delta NO_{xi}) \quad (2-12)$$

It is important to note that this calculation results in the true reactor potential value accounting for the actual flue gas flow rate and blockage values, not a calculated quantity based on the design area velocity and an estimate of the blockage.

2.4 Laboratory Versus *In situ* Determination of Reactor Potential and Catalyst Activity

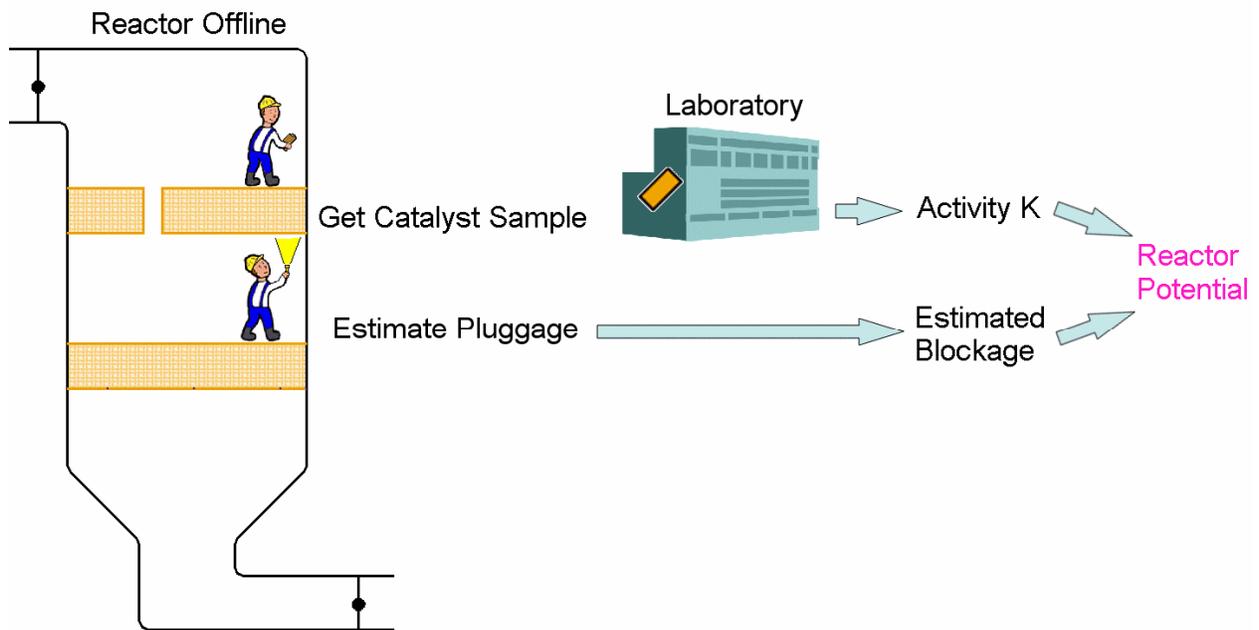
The prior two subsections described the current practice of determining catalyst activity and reactor potential, as well as the new *in situ* approach. While superficially the measurements appear similar (except for the fact that the *in situ* measurement is performed in the full-scale reactor), there are some fundamental differences that warrant discussion.

The differences in these two approaches are illustrated in Figure 2-2. For catalyst management one needs to know the overall reactor potential. In the traditional approach (Figure 2-2a), a laboratory measurement is made of the catalyst activity K . The reactor potential is then calculated using an estimate of the blockage of each layer along with the design area velocity. If the estimate of blockage is inaccurate, or if the actual flue gas flowrate differs from the design value, the calculated reactor potential will be in error.

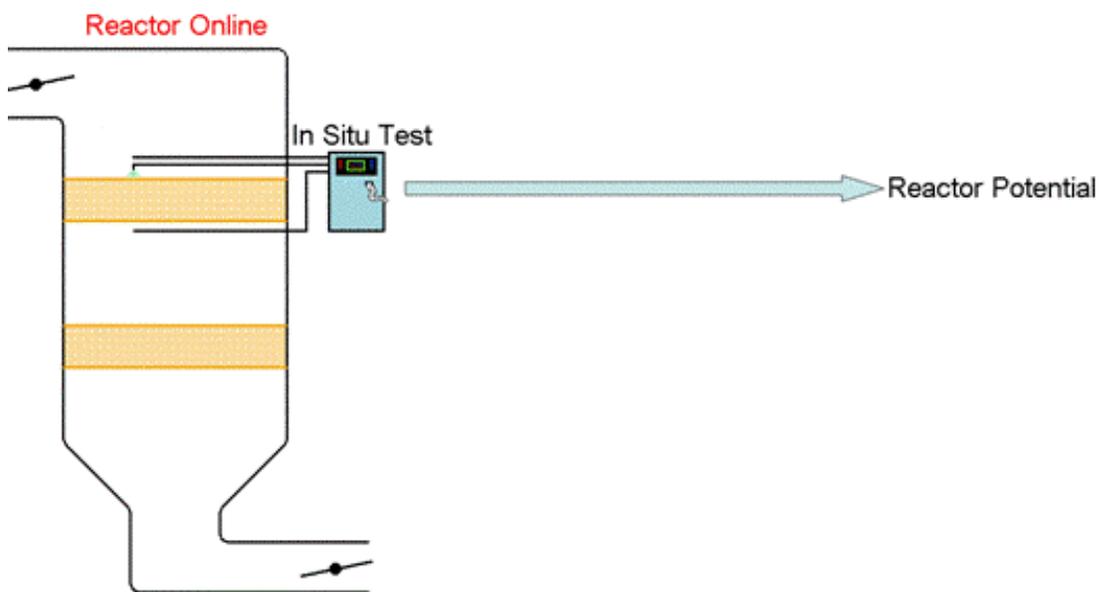
On the other hand, the *in situ* approach provides a direct measurement of the actual reactor potential (Figure 2-2b). This measurement inherently accounts for the actual flue gas flowrate, and the actual blockage of the catalyst layer.

If one wanted to determine the catalyst activity from the *in situ* measurement then an estimate of the blockage and the design area velocity would be used to calculate K_i (Figure 2-3) utilizing the following relationship.

$$K_i = \frac{RP_i A_{vi}}{(1 - B_i)} \quad (2-13)$$



(a) Traditional Laboratory Determination of Reactor Potential



(b) *In situ* Determination of Reactor Potential

Figure 2-2. Laboratory and *In situ* Determination of Reactor Potential

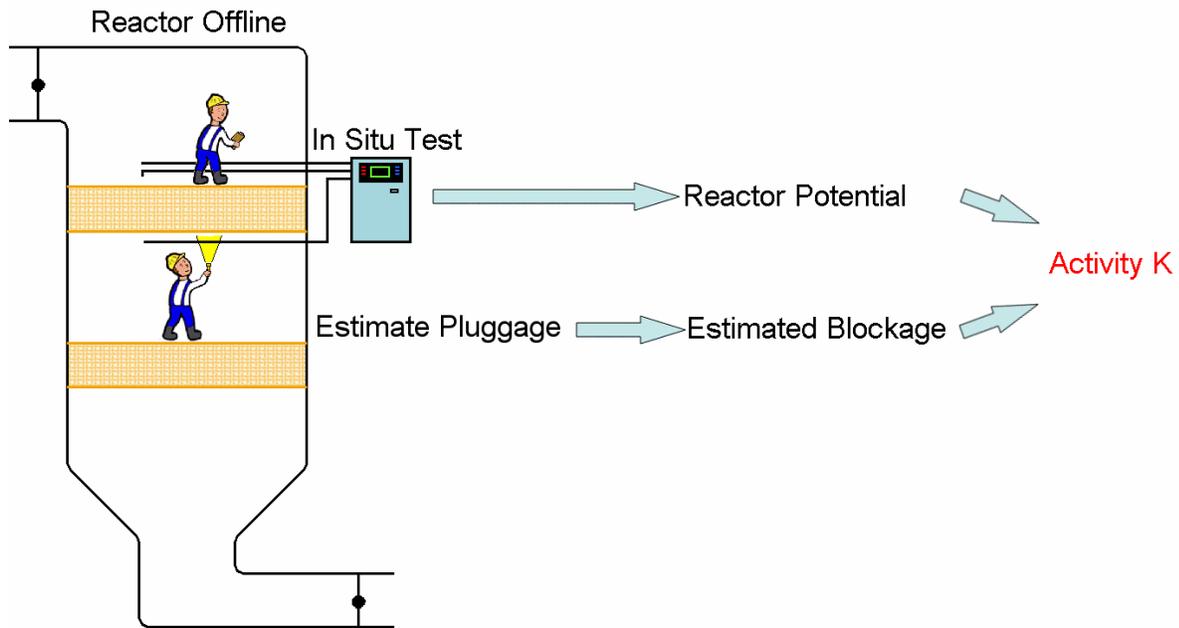


Figure 2-3. Determining Catalyst Activity from the *In situ* Reactor Potential Measurement

3

FIELD DEMONSTRATION

The field demonstration of the *in situ* catalyst activity measurement methodology is taking place over the 2005 and 2006 ozone seasons at Alabama Power Company's Plant Gorgas Unit 10 SCR reactor.

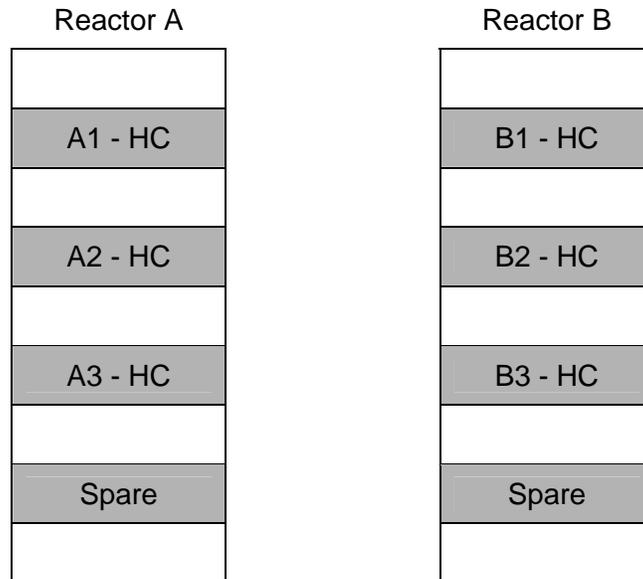
Gorgas Unit 10 is a 700 MW tangentially-fired boiler that started operation in 1972 and burns an Alabama bituminous coal. The unit was retrofit with an SCR system that began ozone season operation in May 2002. The Gorgas Unit 10 system is a 3 + 1 design with two separate reactors (A and B). Three layers of extruded honeycomb catalyst were initially installed with room for a spare layer. Prior to the start of the 2006 ozone season, a new layer of plate catalyst was added to the top layer, and the "used" top layer was moved down to the fourth (spare layer) location in the other reactor. In this move, the top layer in the A reactor was moved to the bottom layer in the B reactor, and vice versa. This is illustrated in Figure 3-1.

The *in situ* measurements began at the start of the 2005 ozone season. At this time the original three layers of honeycomb catalyst in each reactor had accumulated nominally 11,500 hours of operating time.

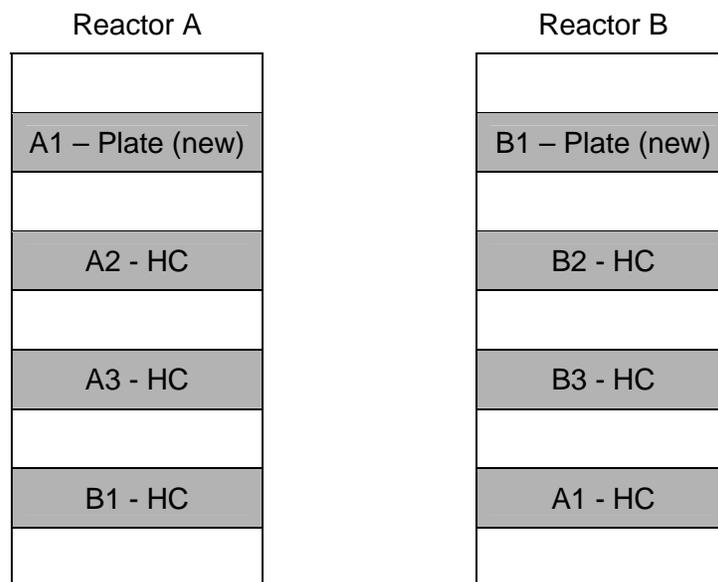
The *in situ* measurement program is being performed in two phases, each comprising a full ozone season. The first phase during the 2005 ozone season was a proof-of-concept phase. Three *in situ* activity modules were installed in the B reactor, one on each of the three original catalyst layers. A portable, electrochemical-based NO and O₂ emissions analysis system was used to measure the activity on a monthly basis throughout the 2005 ozone season. The primary objective of this proof-of-concept phase was to determine the overall viability of the *in situ* measurement approach. This report documents the results of the proof-of-concept tests conducted in 2005.

Following the 2005 proof-of-concept tests, the second phase of the testing will take place during the 2006 ozone season. This test phase will involve adding additional test modules to the B

reactor such that there are two modules on each of the four catalyst layers (3 honeycomb and 1 plate), for a total of eight test modules. In addition, a more commercial version of the



(a) Initial Catalyst Loading (HC = honeycomb)



(b) Catalyst Addition Prior to 2006 Ozone Season

Figure 3-1. Gorgas Unit 10 Catalyst Arrangement

measurement and control system will be designed and fabricated. This will include an integrated system with data acquisition and control equipment that will allow activity testing to be performed remotely, via the internet. In addition, the emissions analysis system will be upgraded to include chemiluminescent NO and zirconium-oxide O₂ analyzers.

4

IN SITU TEST RESULTS

The goal of the *in situ* test methodology is to measure the reactor potential of each layer under the operating conditions of the full-scale SCR reactor. This is accomplished by creating a small region on each layer where the NH_3/NO_x ratio is greater than 1, thereby allowing the measurement of the maximum NO_x removal across the catalyst, and thus the direct determination of the reactor potential for that particular layer. While the host-unit boiler is not in any way controlled during these tests (i.e. load blocked), the tests are run during full-load operation in order to best emulate the SCR design conditions (i.e. the design A_v).

As indicated previously in Section 2, since the *in situ* reactor potential measurements are performed on the full-scale SCR, the results reflect the true operating conditions and NO_x removal performance of the SCR reactor accounting for the effects of catalyst deactivation, blockage of the individual layers, and the actual flue gas flowrate through the catalyst.

One significant difference in between the *in situ* and laboratory methods is that the *in situ* technique is not as controlled or spatially well-defined. In the laboratory, it is relatively easy to set an NH_3/NO_x ratio of 1.0 or 1.2 since the gas flowrates are all well controlled and catalyst test sample is completely enclosed in a housing. With the *in situ* test module, there are no walls to prevent the additional NH_3 injected via the test module AIG from diffusing out from the test area. Thus, simply setting the test NH_3/NO_x ratio to 1.0 based upon the bulk flue gas flowrate and the NO_x concentration at the inlet of the test section, does not guarantee the point of maximum NO_x removal will be achieved. Furthermore, there may be excess, unreacted NH_3 from the host unit's AIG that has passed through the catalyst layer above, and is now entering the test region on the layer below. For these reasons, the NH_3 flowrate required to achieve the maximum NO_x removal point cannot be calculated, but rather must be determined experimentally for each individual *in situ* test location.

As described previously, NO_x removals were measured using electrochemical-based sensors for O_2 and NO only. Ammonia and NO_2 were not measured during the test program. Gas

sampling was conducted at the inlet and outlet of each test module as indicated in Figure 2-1. The portable gas analysis package housed two separate O₂ and NO analysis systems, allowing the simultaneous measurement of inlet and outlet conditions.

4.1 Initial *In situ* Test Protocol

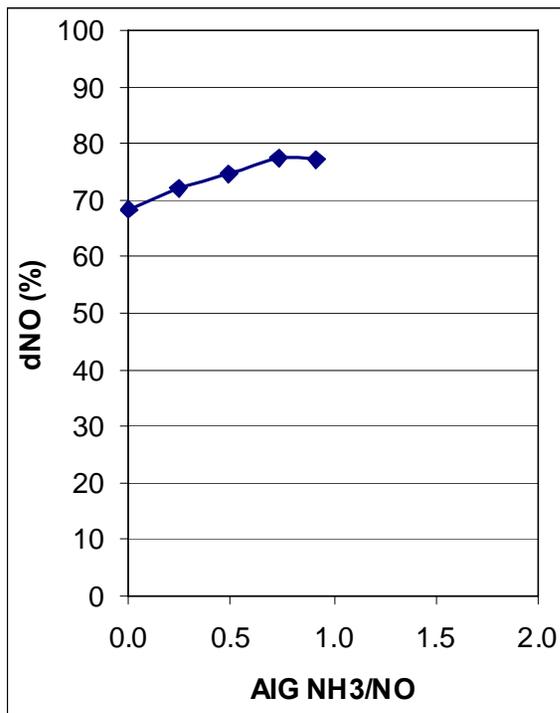
To best characterize the NO_x removal response as a function of NH₃ injection rate, a specific testing protocol was followed for each *in situ* test location during the initial phase of tests run during the 2005 ozone season. First, the NO removal across the test module was measured without any additional NH₃ injection through the module AIG. Once this baseline NO_x removal was characterized, NH₃ was added incrementally via the test module AIG and the NO_x removal monitored until the point of maximum NO_x removal was achieved. Once the maximum NO_x removal was determined, the reactor potential for the catalyst layer was calculated via:

$$RP_i = -\ln(1-\Delta NO_{xi}).$$

Figure 4-1 presents the results of a typical set of NO_x removal measurements utilizing the test protocol outlined above. For each of the three test locations, the NO_x removal is presented as a function of the test module NH₃/NO_x ratio, which is calculated based upon the NH₃ injected through the test module AIG only (i.e. does not include the NH₃ already in the flue gas from the SCR reactor's full-scale AIG). The Gorgas Unit 10 SCR system is typically operated at 85% NO_x removal overall. Figure 4-1 shows that under this condition, the baseline NO_x removal levels across layers 1, 2, and 3 are nominally 68%, 42%, and 8%, respectively. These variations in removal through the reactor are expected as the full-scale AIG is located ahead of the first layer, and while the NO_x levels decrease as the flue gas moves through the reactor, the amount of unreacted NH₃ decreases at a faster rate. Thus, the overall NH₃/NO_x ratio decreases as the flue gas passes through the reactor.

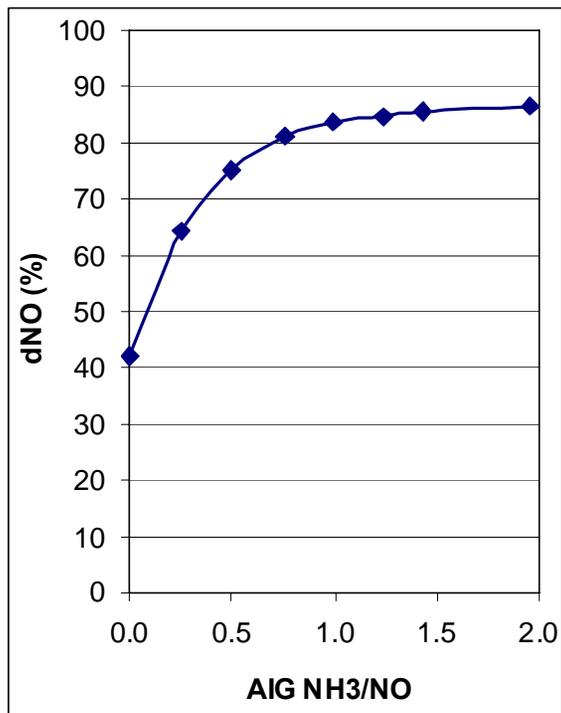
As the NH₃/NO_x ratio is increased at each test location by injecting additional NH₃ via the test module AIG, the NO_x removal for that test location is seen to increase and eventually level out at a maximum value. For the particular set of tests shown in Figure 4-1, the maximum NO_x removal rates are nominally 77%, 87% and 91% for layers 1, 2 and 3, respectively. In multiple-layer, full-scale SCR systems, it is expected that the catalyst deactivation rates will be higher for the "upstream" layers in the reactor, and the maximum NO_x removals shown in Figure 4-1 confirm this expectation. Recall that both K and RP are a function of the relationship: $-\ln(1-\Delta NO_x)$. Thus, as the maximum NO_x removal increases, both the catalyst activity and reactor potential for that layer increase.

Catalyst Layer 1



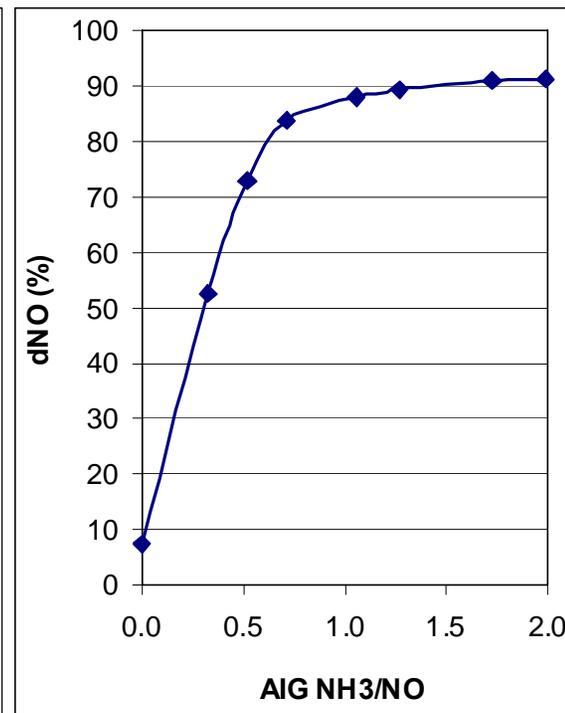
● ΔNO_x maximum = 77.3%

Catalyst Layer 2



● ΔNO_x maximum = 86.6%

Catalyst Layer 3



● ΔNO_x maximum = 91.3%

Figure 4-1. *In situ* NO_x Removal as a Function of NH₃ Injection Rate

4.2 Final *In situ* Test Protocol

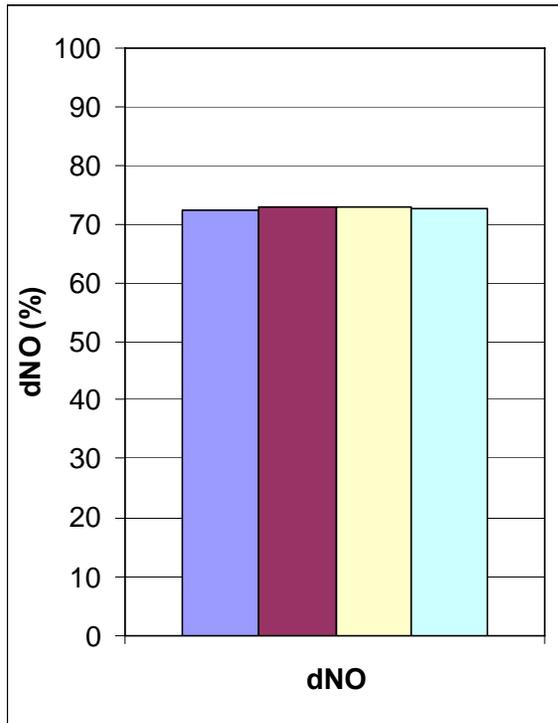
Running the NO_x removal versus NH₃/NO_x ratio curve is a time consuming process, and an entire day is required to run a complete set of tests for each catalyst layer as shown in Figure 4-1. The monthly NO_x removal testing at the Gorgas Unit 10 SCR was conducted over a period of two days, with each day resulting in a NO_x removal curve for each of the three test modules. A review of the first four sets of test results indicated that while the basic shape of the curve was consistent with time for each catalyst layer, the maximum NO_x removals varied slightly. In order to better understand these variations, the daily test protocol for each layer was modified. After the initial baseline NO_x removal measurement, rather than incrementally increase the NH₃ injection rate, the injection rate was set at a value high enough to assure reaching the maximum NO_x removal point, and then four to five repeat tests were run at this condition. The “high” NH₃ injection rate for these tests was determined by reviewing the multiple NO_x removal curves previously collected the individual catalyst layer.

Figure 4-2 presents the results of a typical set of NO_x removal measurements utilizing the modified test protocol outlined above. The tests for each catalyst layer were conducted over a time span of one to two hours, and results indicate very little variation in the NO_x removals measured over that period of time. The average NO_x removals measured for catalyst layers 1, 2, and 3 were nominally 73%, 80% and 86%, respectively. The specific set of data shown in Figure 4-2 was collected at the end of the 2005 ozone season, and it can clearly be seen that the average maximum NO_x removals for each layer have decreased from the levels measured early in the test program (i.e. Figure 4-1), indicating that both the catalyst activity and reactor potential for each layer have decreased.

4.3 Summary of 2005 *In situ* Test Results

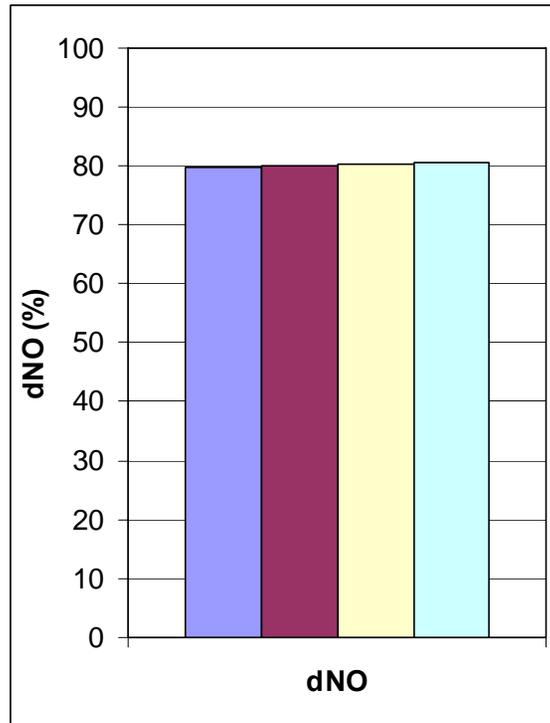
Site visits were conducted on a monthly basis throughout the 2005 ozone season in order to monitor the reactor potential of each the three catalyst layers. The outcome of this set of tests is shown in Figure 4-3, where the results are presented on the basis of relative reactor potential (RP/RP₀) versus operating hours. RP₀ is defined as the reactor potential corresponding to when the catalyst was new and freshly installed in the reactor. Recall the Gorgas Unit 10 SCR reactor began operation in May of 2002 for that year’s ozone season. Thus, all three catalyst layers had accumulated nominally 11,500 hours of exposure prior to the start of the *in situ* test program beginning in May of 2005. For the purposes of this test program, RP₀ is calculated based upon the new catalyst activity (K₀) measured by Southern Company’s third-party catalyst

Catalyst Layer 1



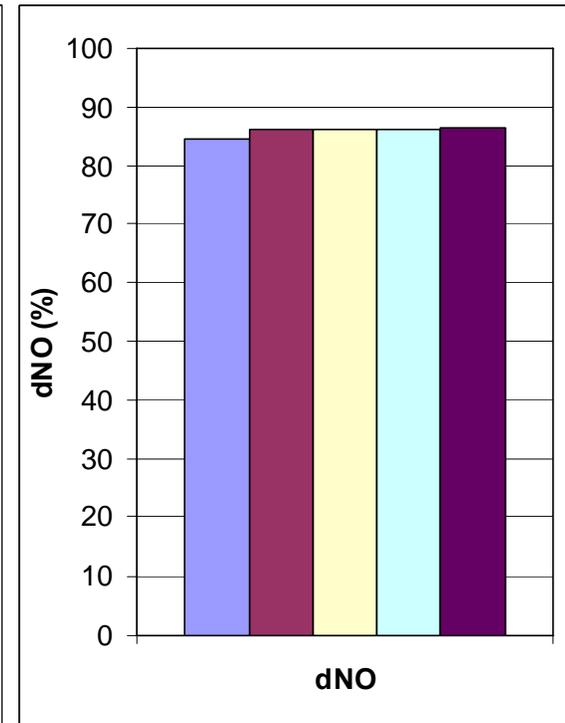
• ΔNO_x average = 72.7%

Catalyst Layer 2



• ΔNO_x average = 80.2%

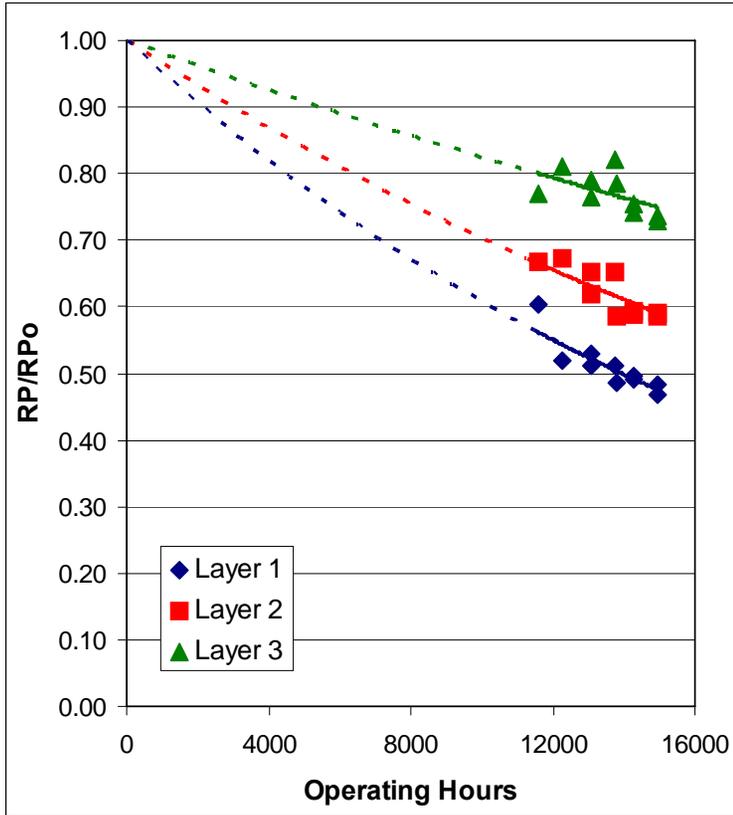
Catalyst Layer 3



• ΔNO_x average = 85.7%

Figure 4-2. Typical Repeatability of *In situ* NO_x Removal Test Results

Individual Layers



Overall Reactor

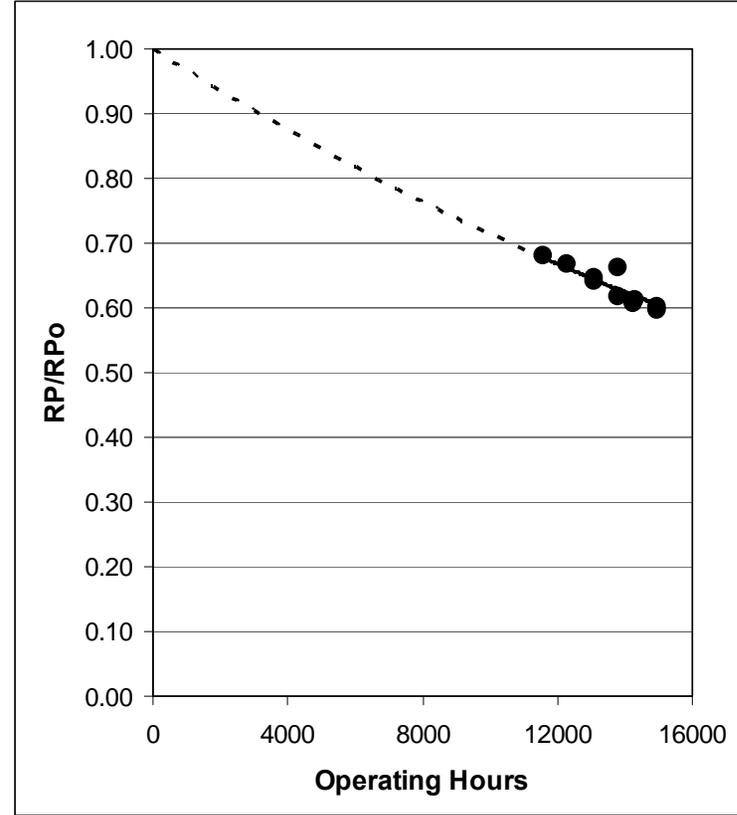


Figure 4-3. Summary of *In situ* Reactor Potential Results for 2005

testing organization, and the Gorgas Unit 10 SCR design area velocity. The results are presented on the basis of RP/RP_0 in order to avoid revealing the actual RP data, which Southern Company considers business confidential.

Figure 4-3 presents the reactor potential results for the individual catalyst layers, as well as for the entire reactor overall. As would be expected, the results indicate the reactor potential for first layer is the lowest, and the potential for the third layer is the highest. While the results for each catalyst layer exhibit some scatter, the trends for each layer are clear. All three layers show an obvious decline in reactor potential over the course of the 2005 ozone season. On an overall basis, the results show the potential for the entire reactor decreased from nominally 0.68 to 0.60 during the five-month test period. This ending reactor potential number (60% of the value when new) may seem low considering SCR vendors generally define end-of-life for the catalyst as K/K_0 (or sometimes RP/RP_0) equal to 0.60 or 0.65. However, it is interesting to note that Southern Company chose to add the new fourth layer of catalyst to the Gorgas Unit 10 reactor during the outage between the 2005 and 2006 ozone seasons. This decision was not based on the *in situ* measurements, but rather based on the results of the annual third-party analysis of physical catalyst samples removed from the reactor. The results of these third-party analyses will be discussed, as well as compared to the *in situ* results, in the following section.

5

LABORATORY TEST RESULTS

As mentioned in Section 2, an important part of a utility's catalyst management program is the removal of physical samples from the reactor, and their subsequent analysis by either the original catalyst vendor or a third-party testing organization. For the Gorgas Unit 10 SCR, Southern Company personnel remove a test sample from each layer of catalyst in both reactors at the end of each ozone operating season. Generally, these samples are removed in October and are then sent to the third-party testing organization responsible for catalyst testing for all of Southern Company's SCR systems. These laboratory analyses result in an assessment of the catalyst activity (K_i) for each of the samples submitted. To compare the results of the lab analysis to the in situ data, an estimate of the blockage (B_i) for each catalyst layer is needed to calculate the reactor potential (RP_i) for each layer per equation (2-10):

$$RP_i = \frac{K_i (1 - B_i)}{A_{vi}^{clean}}$$

Laboratory results from two sets of samples were available to compare to the in situ measurements performed in 2005. First, the set of catalyst samples removed at the conclusion of the 2005 ozone season combined with blockage estimates from the end of 2005 would be appropriate for calculating a reactor potential value for the close of the 2005 season. Second, the set of samples removed at the conclusion of the 2004 ozone season combined with blockage estimates from the beginning of the 2005 would be appropriate for calculating a reactor potential value for the start of the 2005 season.

5.1 Laboratory Determination

Table 5-1 summarizes the results of the third-party catalyst activity analysis of the samples removed from the reactor at the conclusion of the 2004 and 2005 ozone seasons. The results are presented on the basis of K/K_0 in order to avoid revealing the actual activity (K) data, which Southern Company considers business confidential. An important thing to note with respect to these results is that in each case, the data indicate the catalyst activity increased

Table 5-1. Laboratory Relative Activity Test Results

| Date | K/K₀ Layer 1 | K/K₀ Layer 2 | K/K₀ Layer 3 |
|--------------|--------------------------------|--------------------------------|--------------------------------|
| October 2004 | 0.71 | 0.75 | 0.79 |
| October 2005 | 0.80 | 0.78 | 0.90 |

from 2004 to 2005. The third-party testing organization provided data indicating that while the 2005 results were consistent with deactivation rates seen from the analysis of samples removed at the conclusion of the 2002 and 2003 ozone seasons, the 2004 activity results fell notably below the expected levels. The reason for the difference in the deactivation rates indicated by the 2004 data and the rest of the third-party test results is not understood at this time. It has been postulated that variations in the catalyst activity across a single layer may be responsible for at least part of this difference.

5.2 Visual Blockage Estimates

Generally, estimating the blockage for each layer is a manual process that is performed at the same time the catalyst samples are removed at the end of each ozone season. The process consists of having personnel physically enter the reactor, and then count the number of blocked passages for a “representative sampling” of the number of catalyst modules in the layer. The blockage ratio calculated from the sample is then applied for the entire catalyst layer. Due to the overall size of the SCR reactor and the number of catalyst modules in each layer (for example, a single layer in just one reactor of the Gorgas Unit 10 SCR contains 98 catalyst modules that measure nominally 3 feet by 6 feet), a “representative” sample generally consists of less than 20% of the modules. Thus, these assessments of blockage can only be considered estimates, at best.

Table 5-2 summarizes the blockage estimates resulting from the visual inspections performed by Southern Company personnel at the conclusion of the 2004 and 2005 ozone seasons. Given the nature of how these visual assessments are conducted, even Southern Company personnel believe that the blockage numbers estimated with this technique are likely only accurate to 10% to 15%, on an absolute basis. The results summarized in Table 5-2 illustrate this in two different areas. First, unless there was a replacement or exchange of catalyst layers during the outage between ozone seasons or some other work performed to affect the flue gas

flow through the reactor, one would expect to see somewhat similar levels of blockage on a year-to-year basis. The results

Table 5-2. Visual Estimates of Catalyst Layer Blockage

| Date | Layer 1 | Layer 2 | Layer 3 |
|--------------|----------------|----------------|----------------|
| October 2004 | 21% | 14% | 12% |
| October 2005 | 20% | 30% | 25% |

from 2004 and 2005 indicate notable variations in blockage for catalyst layers 2 and 3. Additionally, the general expectation is that ash build-up and blockage will be highest on the first layer, and then decrease as the flue gas flows through the reactor. The results for 2005 indicate the blockage on the first layer was lower than that for either of the two subsequent layers. In situ cleaning of the catalyst layers with compressed air is also performed after each SCR operating season. This affects the catalyst cleanliness and therefore the estimated blockage.

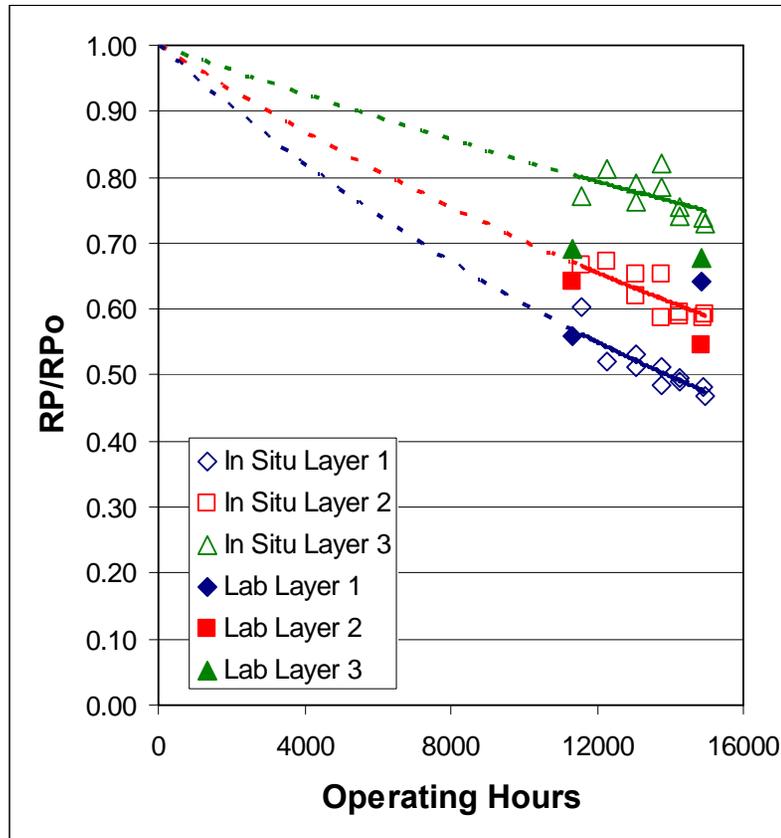
Utilizing the laboratory catalyst activity data and the blockage estimates provided in Table 5-2 above, reactor potential values for each catalyst layer may be calculated for both the beginning and end of the 2005 ozone season. These results are presented on the basis of RP/RP_0 in Figure 5-1, which for comparison purposes also includes the *in situ* test results for the same period of time. In general, the agreement between the laboratory and *in situ* results is less than satisfactory. While there is reasonable agreement for catalyst layer 2 at both the start and end of the ozone season, the laboratory values for layer 3 are notably below the *in situ* values, and the laboratory values for layer 1 indicate a significant increase in RP over the course of the ozone season.

5.3 Alternate Blockage Assessment

As indicated in the discussions above, the visual assessment technique for determining the catalyst layer blockage values is an estimate at best. Unfortunately, the laboratory reactor potential calculation is highly dependent on this value. In an attempt to improve the accuracy of the laboratory RP calculation, a secondary method of determining blockage was investigated. Namely, the change in pressure drop across the catalyst layer, relative to when the layer was new, should provide another means of tracking blockage. Plant personnel were able to provide a data file consisting of 5-minute average data points for the pressure drop across each of the three catalyst layers for the entire 2005 ozone operating season. From this data the average full-load pressure drop at both the beginning and end of the season was calculated for each

catalyst layer. Plant personnel were also able to provide a similar data file for 2002, the initial operating season for the Gorgas Unit 10 SCR system. This second file provided a means to determine the full-load pressure drop when the catalyst was new and had no blockage.

Individual Layers



Overall Reactor

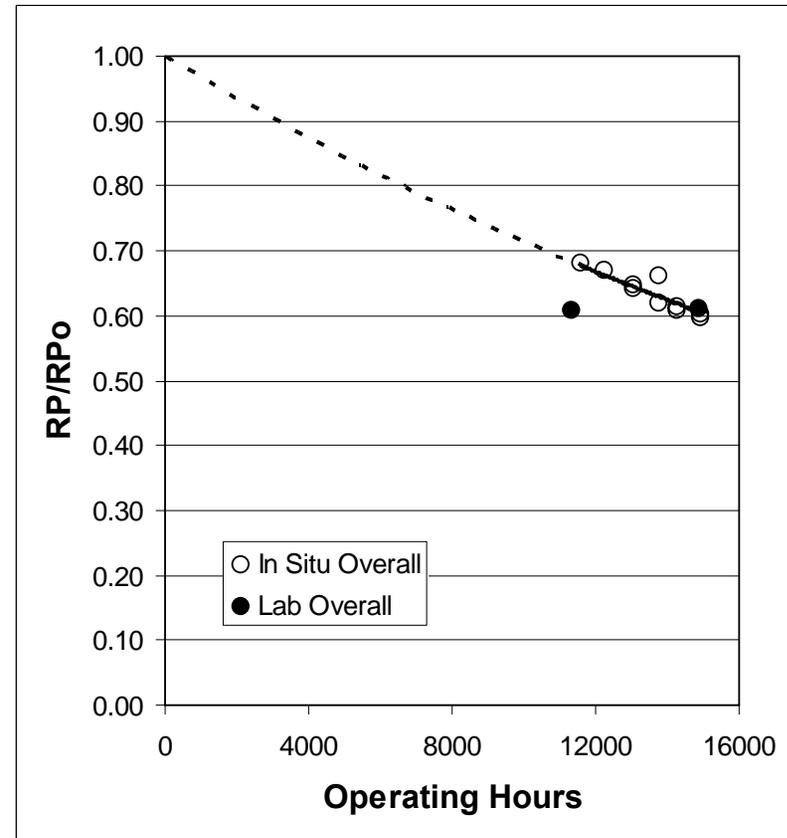


Figure 5-1. Comparison of Laboratory and *In situ* Reactor Potential Results (Laboratory Values Based on Visual Blockage Estimates)

Table 5-3 shows the blockage values calculated from the increase in pressure drop measured across each layer. Plotting of the entire 2005 pressure drop data set for catalyst layers 1 and 2 indicated that while the pressure drop varies throughout the day (likely due to unit load variations), overall there was a steady increase over the course of the five-month period. While the data for layer 3 showed the same general trends as the other layers at the beginning, later in the season there were a number of very uncharacteristic spikes and step-like changes indicating the development of some sort of operational issue with that particular pressure transmitter. Since the operation of the transmitter was in question, there is no final data point for layer 3 included in Table 5-3.

Table 5-3. Catalyst Layer Blockage Values Based on Pressure Drop Increase

| Date | Layer 1 | Layer 2 | Layer 3 |
|--------------|----------------|----------------|----------------|
| October 2004 | 19% | 19% | 10% |
| October 2005 | 40% | 24% | n/a |

While the data in Tables 5-2 and 5-3 indicate only one “large” difference between the blockage values resulting from the visual assessment and pressure drop methods (namely the October 2005 data for Layer 1), the remaining data all seem to agree within 5% on an absolute basis. However, the scale of these “small” differences is misleading. For example, the difference between 14% and 19% blockage for Layer 2 in 2004, is nominally a 30% difference on a relative basis. Since the reactor potential calculation is directly dependent on the blockage value (recall equation 2-10), a 30% difference in B results in a 30% difference in the final RP value.

Intuitively, the pressure drop method would certainly seem to be more accurate than a visual estimation. In order to provide a “sanity check” on this intuitive assessment, a third method of inferring the pressure drop was investigated consisting of the following steps:

- Assume the *in situ* assessment of RP is correct, as it is a direct result of the maximum NO_x removal measurement in the full-scale SCR reactor.
- Assume the laboratory assessment of K is correct, as the conditions of the measurement are tightly controlled and the NO_x removal can be accurately determined.
- Since the design A_v for the full-scale reactor is known, the blockage can be determined from equation 2-10.

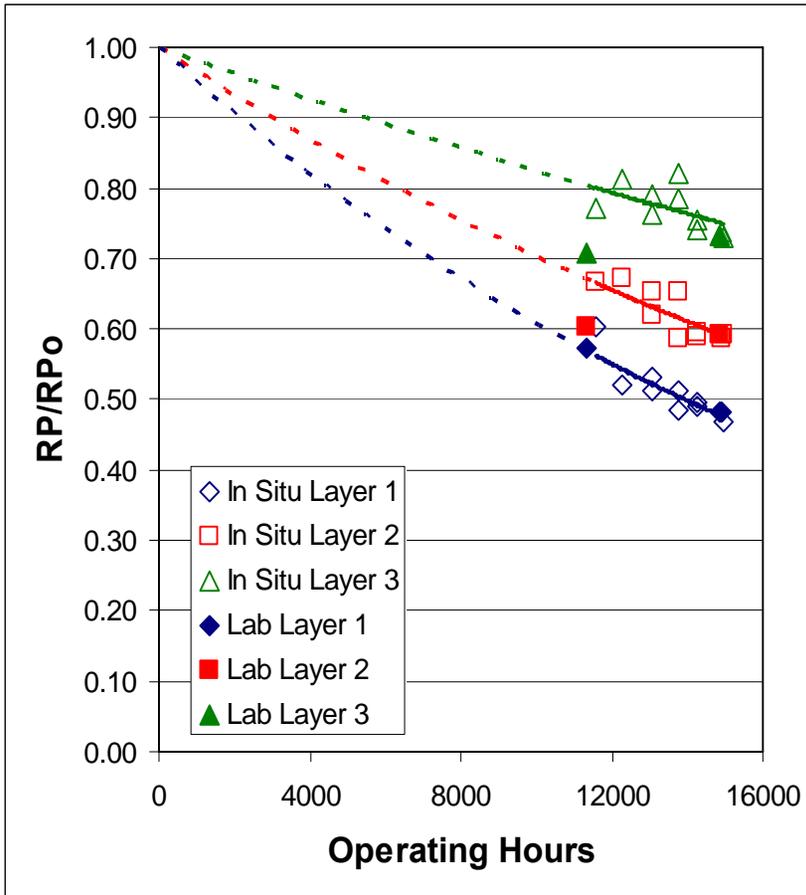
Table 5-4 compares the results of the analysis outlined above with the results of the visual assessment and pressure drop methods for all three catalyst layers at the end of the 2005 ozone season. The comparison clearly indicates the pressure drop method is preferred over the estimate based on a visual inspection.

Table 5-4. Comparison of Blockage Value Calculation Methods (October 2005)

| Method | Layer 1 | Layer 2 | Layer 3 |
|-------------------------|----------------|----------------|----------------|
| Plant Visual Inspection | 20% | 30% | 25% |
| Pressure Drop Increase | 40% | 24% | n/a |
| Calculate from RP and K | 41% | 24% | 19% |

Figure 5-2 presents the results of the laboratory reactor potential calculations utilizing the blockage values resulting from the pressure drop analysis. Note the blockage value for layer 3 at the end of the season was assumed to be 19% based upon Table 5-4 above. The laboratory and *in situ* reactor potential values at the conclusion of the ozone season show significantly improved agreement relative to that seen utilizing the visual blockage assessment (Figure 5-1). Unfortunately, the agreement for layers 2 and 3 at the beginning of the season is still less than desired. However, given the issues previously raised regarding the 2005 laboratory activity data upon which the RP values are based, only limited agreement should be expected.

Individual Layers



Overall Reactor

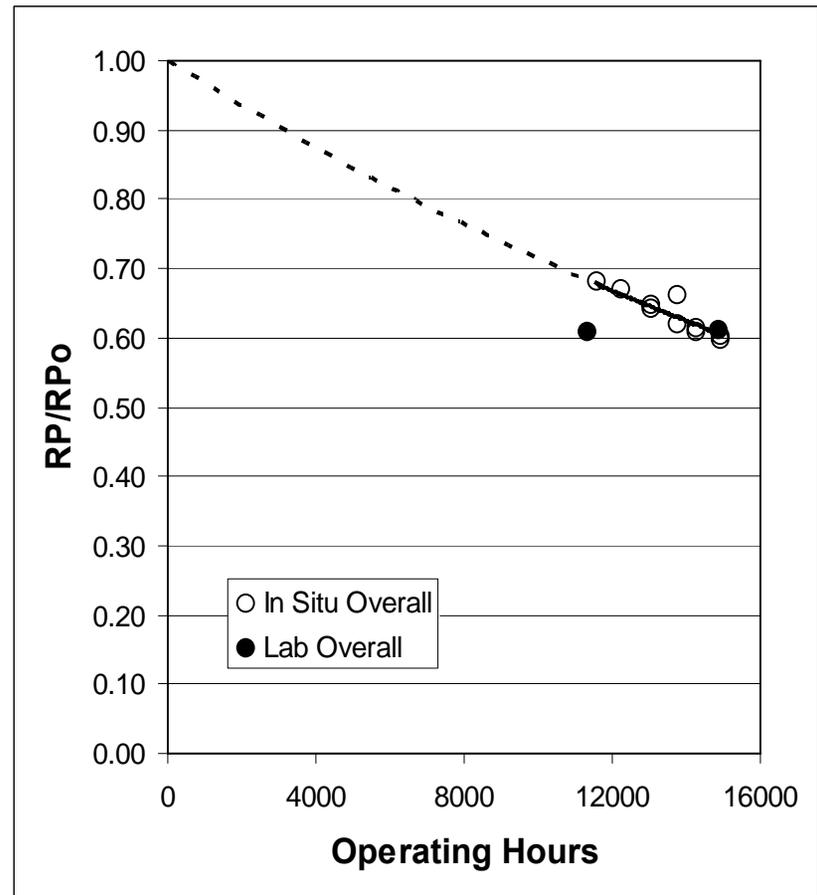


Figure 5-2. Comparison of Laboratory and *In situ* Reactor Potential Results (Laboratory Values Based on Pressure Drop Increase)

6

SUMMARY

The preceding discussions of *in situ* and laboratory measurement techniques showed that while in some instances the reactor potential values resulting from the two methodologies agree quite well, at other times the agreement is far from satisfactory. Therefore, it is of value to discuss the reasons why the results of the two methodologies might differ.

The basis of the laboratory technique is the measurement of catalyst activity at the design area velocity condition. These values of K and A_v , along with a blockage estimate, are then utilized to calculate reactor potential for each catalyst layer. As already discussed at length, the accuracy of the blockage estimate is critical to the precision of the resulting value of RP, and the traditional visual assessment of blockage will not provide the required accuracy. A preferred method would be to calculate the blockage from the increase in pressure drop across the catalyst layer. Another potential area of inaccuracy in the laboratory analysis is that the actual flue gas flow rate in the full-scale SCR reactor may differ from the design flow. This difference can result from changes in fuel specification or overall boiler operating parameters. If this is the case, the area velocity utilized in the laboratory RP calculation will be in error.

The *in situ* determination of reactor potential depends only on the measurement of the maximum NO_x removal across the test module, and of course conducting the test at full-load conditions. An additional advantage is that the *in situ* technique measures the RP for the same piece of catalyst, every time, year after year. With the laboratory technique, a different sample is removed from the catalyst layer during each sampling opportunity. Therefore, if there are any spatial differences in activity across a layer, the calculated RP values from the laboratory analysis will also reflect this variability.

A final area where differences could be introduced into the reactor potential results from the two techniques is in the NH_3/NO_x ratio at which the tests are run. In the laboratory device, the activity tests are conducted at NH_3/NO_x equal to 1.0 or 1.2 (depending on the size of the catalyst sample). With the *in situ* technique, NH_3 is added until NO_x removal reaches a maximum value.

The “true” *in situ* NH₃/NO_x ratio could be as high as 1.5 to 1.8, but as discussed previously the value is difficult to determine accurately due to the existing NH₃ in the flue gas stream, as well as the inability to prevent the NH₃ introduced through the test module AIG from migrating away from the test area. Operating at NH₃/NO_x ratios in excess of 1.0 or 1.2 may result in slightly higher NO_x removals, and thus slightly higher RP values. However, when presented on the basis of RP/RP₀, the results from the two methods should be the same.

Both the laboratory and *in situ* test methodologies have advantages and disadvantages as indicated in Table 6-1. Overall, an important point to note is that the *in situ* technique should not be thought of as a replacement for the laboratory analysis of catalyst samples, but rather a companion measurement as the *in situ* measurement can not be used to determine causes of catalyst deactivation such as is achievable with surface and bulk analyses from laboratory samples.

Table 6-1. Comparison of Measurement Techniques

| Laboratory | <i>In situ</i> |
|--|--|
| <p>Pro</p> <ul style="list-style-type: none"> • Provides accurate K determination • Sample removed may also be analyzed for physical and chemical properties (surface area, poisons, etc.) | <p>Pro</p> <ul style="list-style-type: none"> • Direct measurement of RP • Larger data set (testing is not dependent on outage schedule) • Can test immediately after unit upset (e.g. tube leak) to assess effect on SCR operation |
| <p>Con</p> <ul style="list-style-type: none"> • Relies on an estimate of blockage to calculate RP • Limited data set (samples can only be removed during outages) | <p>Con</p> <ul style="list-style-type: none"> • Need a blockage estimate to calculate K • ΔNO_x increase at NH₃/NO_x >1 may yield slightly higher absolute RP values |