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Fuel Effects on Catalyst Life and Deactivation Database

Three Case Studies with Plate Type Catalysts

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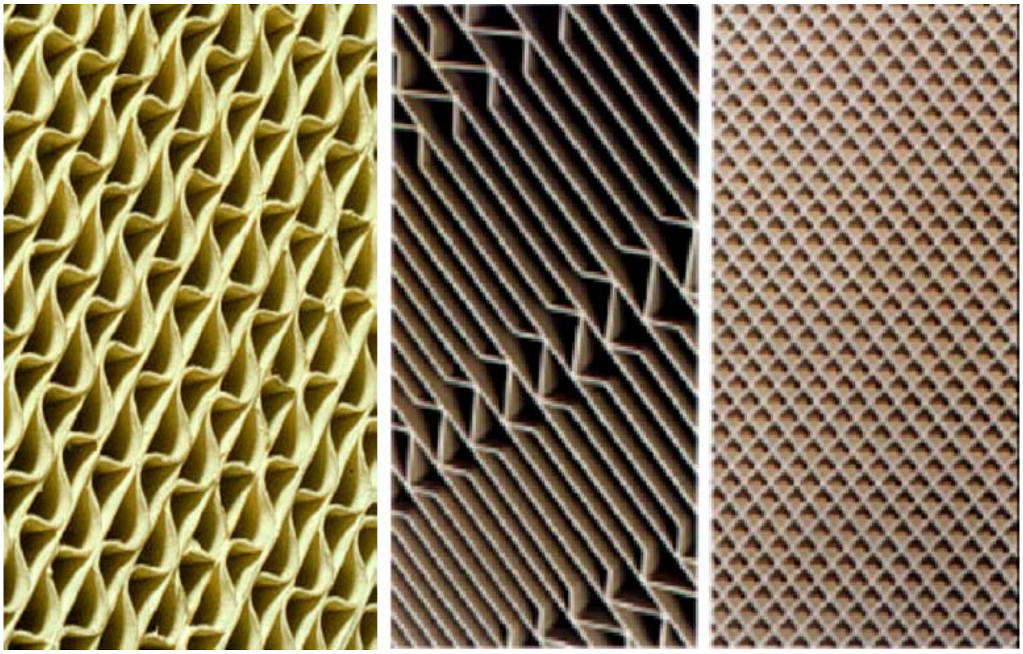

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Technical Update, December 2009

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REPORT SUMMARY

This report provides case studies and catalyst performance supplemental data to aid EPRI members in the management of Selective Catalytic Reduction (SCR) installations, particularly as related to the firing of both PRB and bituminous coals. The report discusses the primary deactivation mechanisms, along with analytical techniques to help members identify the primary modes of deactivation in their specific catalyst fleet. In addition, it offers benchmark data about the deactivation rates expected depending on fuel composition. The information is extremely helpful for estimating catalyst deactivation rates, determining the impact that various fuels will have on deactivation, and developing deactivation mitigation strategies.

Background

Exposure to various constituents in the gas stream causes SCR catalyst activity to degrade with time. While catalyst vendors provide utilities with guaranteed SCR performance in terms of NO_x reduction and ammonia slip for a certain number of hours of operation, actual SCR performance can and will vary, and is primarily dependent on coal characteristics. This variation in performance can make it difficult to determine appropriate catalyst replacement strategies. This report compiles SCR catalyst deactivation information into a single comprehensive database, and investigates the impacts of fuel characteristics and SCR operating conditions on deactivation.

Objectives

- To compile SCR catalyst deactivation information into a single comprehensive database and investigate the impacts of fuel characteristics and SCR operating conditions on SCR catalyst deactivation.
- As more data becomes available, the ultimate goal will be to develop a tool for predicting catalyst life, improve catalyst management plans, and develop best practices to enhance catalyst longevity

Approach

The project team collected deactivated catalyst data from EPRI members of the Post-Combustion NOx Control Program. They also generated additional information at Enonik's bench-scale test facility, in accordance with the VGB catalyst testing protocol. The project team conducted several case studies based upon the database information. Specifically, this report concentrates on the fuel impacts on plate-type catalyst. Researchers divided the analyses by fuel type, including PRB Coal applications, Illinois Basin Coal applications, and Eastern Bituminous Coal applications. In addition to these case studies, the project team completed a correlation analysis reflecting the relationship between catalyst sample arsenic level and deactivation rate.

Results

Results showed that phosphorous poisoning was the controlling deactivation mechanism for PRB fuel. Data indicated that the initial period of flue gas exposure, up to several thousand hours, produced an accelerated rate of catalyst deactivation, dropping to a relative activity of 50%.

After the initial exposure period, the deactivation rate decreased, possibly due to phosphorous saturation, remaining at 3% in the bulk of the catalyst. The analysis showed that phosphorous levels and DeNOx activity was the same for the first and second layers. Researchers need more data to ascertain the impacts of phosphorous on catalyst deactivation, including the deactivation effects on other catalyst types such as honeycomb and corrugated.

With bituminous coals, the primary mode of deactivation will be arsenic poisoning. The data showed that phosphorus poisoning was also a factor with Southern Illinois bituminous fuel. Eastern bituminous fuel with arsenic levels of 10 ppm and ash CaO concentrations of 4.3% gave the most catalyst longevity; catalyst deactivation was 83% after 17,000 hours in service. The project team correlated arsenic concentrations in the catalyst to deactivation rates. The analysis included a total of 12 catalyst samples; all removed from the top layer and from different SCR reactors. Based on this data, they estimated that activity would reach 60% when catalyst arsenic concentrations approximate 22,000 ppmw. The actual arsenic deposition rate will vary according to the application and will largely depend on the arsenic to CaO concentrations.

EPRI Perspective

Overall, the project helped document actual catalyst deactivation mechanisms and rates experienced in the field on a variety of applications. The report clearly demonstrates the value of chemical analysis data in identifying the mechanism of deactivation, and the data helped provide a basis for correlating fuel characteristic and catalyst chemical composition to the rate of deactivation. The information offers a benchmark for comparing various fuels and deactivation rates, and will assist Utilities in determining the impacts that fuels will have on deactivation, helping to maximize catalyst life, and minimize adverse impacts.

Keywords

Selective catalytic reduction (SCR)
Catalyst deactivation
Catalyst poisoning

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1

INTRODUCTION

Background

Catalyst activity degrades with time as a result of exposure to various constituents in the gas stream and is independent of catalyst type and make. While catalyst vendors do provide Utilities with a guaranteed SCR performance in terms of NOx reduction and ammonia slip for a certain number of hours of operation, actual SCR performance can and will vary, and is primarily dependent on coal characteristics. This variation in performance can make it difficult to determine appropriate catalyst replacement strategies. Therefore, the main objectives of this project are to collect actual catalyst deactivation data from Utilities, review past reports and other literature, and analyze the deactivation data with respect to general coal characteristics.

Objectives

The overall objective is to compile SCR catalyst deactivation information into a single comprehensive database and investigate the impacts of fuel characteristics and SCR operating conditions on SCR catalyst deactivation. As more data is generated, the ultimate goal will be to develop a predicting tool to help Utilities project catalyst life, improve catalyst management plans, and develop best practices to enhance catalyst longevity.

Approach

Catalyst data was collected from EPRI members of the Post Combustion NOx Control Program. In addition, Evonik Energy Services was given the task to develop a database of spent SCR catalyst material. Data was generated using bench-scale testing, in accordance to the VGB and EPRI catalyst testing protocols. Information included:

- Catalyst type and SCR operating conditions
- Initial and final NOx activity
- Initial and final SO_2 to SO_3 conversion
- Final catalyst chemical composition
- Fuel and ahs analyses

The current database includes information from 114 catalyst samples collected from 20 different power plants. All catalyst types are well represented and have been deactivated on different fuels and flue gas conditions.

This database will be updated on an annual basis as more catalyst data becomes available. This is especially true of units using unique fuels such as lignite and biomass. Data will continue to be analyzed to investigate the effects of fuel and ash characteristics on catalyst deactivation.

2

CATALYST DEACTIVATION

Catalyst Background Information

SCR catalysts are composed principally of a ceramic-like material which provides the necessary physical pore structure and chemical foundation for the active catalytic components of the catalysts. The ceramic-like material is made up primarily of titania (titanium dioxide, TiO_2), but will include a number of additional components. In the catalyst industry, this ceramic-like material is typically called the catalyst “support.” This term should not be confused, however, with gross support materials, such as metal screens and basket materials, which provide a global physical support structure to the catalyst. In addition to the screens, physical support materials, such as glass fibers, may be utilized.

Catalytically active components of the catalyst include vanadium, molybdenum, tungsten, and various other constituents based on the particular formulation and catalyst manufacturer. SCR catalyst is found in three general types: plate, honeycomb, and hybrid/corrugated. These terms refer to the general physical configuration of the catalyst geometry. Even though the catalysts appear to be quite different from a geometric standpoint, the underlying ceramic portions of the catalysts are quite similar from a bulk composition standpoint. Figure 2-1 shows corrugate, plate, and honeycomb type catalysts from left to right, respectively.

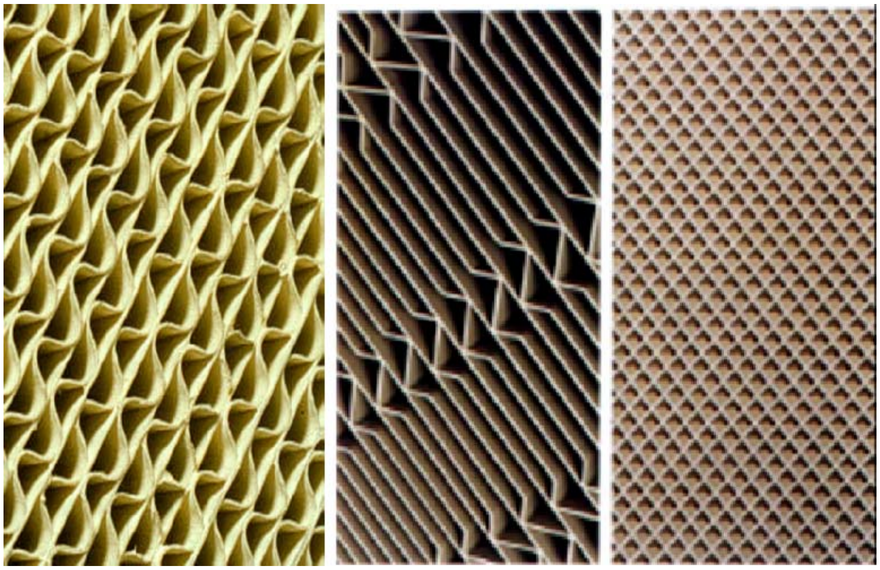

Figure 2-1
Typical Vanadium-Titanium SCR Catalysts, Various Types

Plate Type Catalyst

For plate-type catalysts, the ceramic material is placed on a metal screen. This screen provides structural support to the plate, while the ceramic material provides the needed catalyst porosity and active catalytic component support. Due to the presence of the screen support, plate catalysts have a much larger proportion of bulk metals per unit catalyst mass than do honeycomb or corrugated catalysts. Plate catalysts will typically be heavier on a unit volume basis than their honeycomb and corrugated counterparts. Plate catalysts are manufactured by pressing the malleable, pre-fired, and clay-like ceramic onto the support screen, with subsequent firing/calcining processes used to harden the ceramic. Plate catalysts are characterized by having individual plates of catalyst which are assembled into catalyst modules. The plates are held together by compression and can be removed individually. Glass-like fibers may be added to the ceramic portion of the catalyst and used to help add strength and improve adherence to the screen materials.

Honeycomb Type Catalyst

Most honeycomb catalysts are considered homogeneous, since the ceramic material provides the gross physical support for the catalyst in addition to providing the needed pore structure and active catalytically component support. For most honeycomb catalysts, the chemical composition of the freshly manufactured material will be constant throughout the ceramic material. Honeycomb catalysts are typically manufactured by extruding the clay-like ceramic through a die, forming the honeycomb structure. The “logs” or “elements” of catalyst are then heat-treated, similar to other catalysts.

Corrugated Type Catalyst

Hybrid/corrugated catalysts are formed by using a mat-like fibrous material as physical support. The ceramic material is then applied on and within this mat. Monolithic blocks having a corrugated configuration are then produced, with their physical strength being provided by a combination of both the ceramic material and the fibrous support material. These catalysts are sometimes termed “hybrid” since they have characteristics of both plate and honeycomb catalysts. Unlike true plate catalysts, however, the final bulk catalyst is not composed of individual separate plates, since in the manufacturing process a monolith is formed. This resulting monolithic structure, as well as the absence of a clearly distinguishable support screen, has similarities to honeycomb catalysts, but results in a physical appearance similar to plate.

Table 2-1 shows the typical ranges of components in the ceramic portion of SCR catalysts. As discussed, depending on the catalyst type, additional gross support material may also be present, such as metals from plate catalyst screen support. Each catalyst supplier will have a number of catalyst formulations designed for different flue gas applications, especially as related to the SO_2 conversion requirements for the particular application. Thus, the components present in any particular spent catalyst will vary greatly depending on application, catalyst manufacturer, and specific formulation. Spent catalyst will also contain a large number of trace constituents derived from contact with the flue gas, especially in coal-fired applications. In particular, low levels of arsenic, potassium, sodium, and other metals may be present on spent catalyst associated with coal firing. Fly ash particles will also adhere to the catalyst, adding to the large number of trace components present.

Table 2-1
Typical SCR Catalyst Composition – Ceramic Portion

Component (as oxide)	Concentration (wt%)
Titanium	50-100%
Vanadium	0-10%
Tungsten	0-10%
Molybdenum	0-5%
Silica	0-20%
Other Components	0-20%

Fuel Effects on Catalyst Deactivation

The fuel associated with any particular SCR application will govern to a large degree the design of the catalyst and will dictate the primary deactivation mechanism, the ash loading and characteristics, the flue gas composition, and to a significant degree the potential for fouling. As such, fuel is probably the most important global design parameter that must be addressed with any specific catalyst design. The flue gas composition is, of course, directly related to the fuel being burned, but it should be noted that two units firing identical fuels may produce flue gases which differ somewhat with respect to catalyst deactivation and general performance. Parameters such as SCR operating temperature, ash fineness, metals speciation, oxygen, moisture, and SO_3 levels, etc. will all be influenced by the combustion system design and will in turn influence catalyst performance and deactivation.

Typically, coals are divided into two primary classes based upon their primary mode of deactivation of SCR catalysts. These are: 1) Powder River Basin (PRB) coals, where deactivation is primarily a function of calcium sulfate masking/poisoning and 2) Bituminous coals, where deactivation is typically a function of arsenic poisoning. In both cases, physical fouling issues may override issues associated with classic calcium sulfate or arsenic poisoning. These physical issues include phenomenon such as large-particle-ash (LPA) fouling, which can produce severe loss of functionality of the catalyst very quickly. Thus, for any particular installation, the deactivation mechanisms that actually govern will be highly site specific. Further, with certain fuel blends, it may not be readily apparent which deactivation modes will govern, and as a result, there may be limited confidence in the projections for deactivation.

Certain constituents found in combustion flue gases act as catalyst poisons, and their functioning as such is termed “chemical deactivation” or “chemical poisoning.” These constituents deactivate the catalyst by diffusing into the catalyst pores and attaching to active sites via chemical reactions, thereby preventing the site from participating in the desirable catalytic reaction. In many cases, chemical poisoning represents the main long-term cause of catalyst deactivation for coal-fired units and may also be predominant in heavy oil-fired units. Catalyst poisons include calcium, magnesium, potassium, sodium, arsenic, lead, and some silica forms. For eastern bituminous coals, arsenic is the predominant catalyst poison of interest, while in units firing

Powder River Basin (PRB) coals, calcium/sulfur poisoning is typically cited as the primary poisoning mechanism (these mechanisms are discussed in detail below).

Catalyst Poisoning

Arsenic and Phosphorous Poisoning

In the absence of severe fouling or operational issues, arsenic poisoning is the primary deactivation mechanism for eastern bituminous fuels. Gaseous arsenic (As_2O_3) in the flue gas chemically attacks active vanadium sites, forming a bond which renders the active vanadium site incapable of promoting the deNOx reaction. Figure 2-2 illustrates the deactivation mechanism in which As_2O_3 chemically attaches to active vanadia sites, resulting in a notable reduction in overall catalyst performance. Phosphorous pentoxide (P_2O_5) has the same effect as gaseous arsenic. P_2O_5 is the main chemical deactivation mechanism on PRB applications.[1]

This deactivation mechanism differs from physical mechanisms of deactivation, such as calcium sulfate masking, because there is no aspect of diffusion limitation; pore blockage does not take place – the catalytic vanadium site is simply rendered inactive. Thus, a catalyst that has become poisoned with arsenic may exhibit physical characteristics very close to that of the fresh, but have a severely limited ability to promote the deNOx reaction.

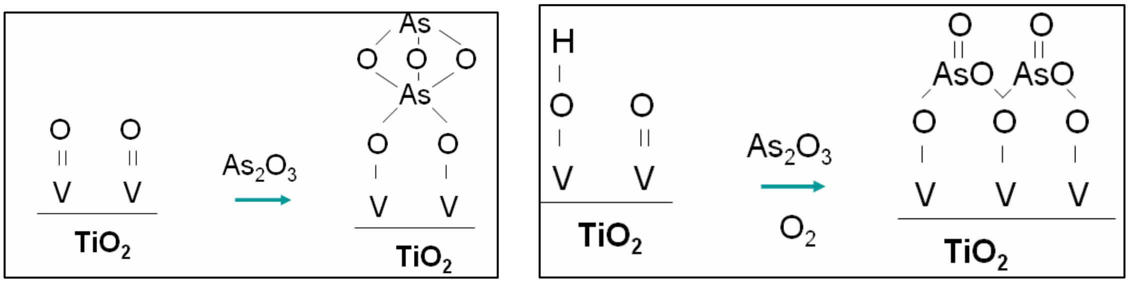

Figure 2-2
Arsenic Poisoning Model[2]

The absolute level of arsenic in the fuel is often considered the controlling factor in the rate of arsenic poisoning (for a given catalyst and installation design). A more applicable parameter is the arsenic-calcium ratio. This is due to the fact that CaO acts as a scavenger for free arsenic. This scavenging effect by calcium helps to reduce the reactive arsenic in the flue gas that would otherwise be available to poison the catalyst. Thus, eastern bituminous fuels with both high arsenic and calcium will not deactivate catalyst as fast as fuel counterparts, which have high arsenic but lower levels of calcium. The addition of limestone to artificially boost fuel calcium levels has been used to mitigate arsenic poisoning in fuels having excessive levels of arsenic. This scheme capitalizes on the ability of the CaO to scavenge the arsenic.

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[1] Assuming that calcium sulfate poisoning/masking is classed as a physical deactivation mechanism. In most PRB applications, both calcium sulfate masking and P_2O_5 poisoning will contribute to the overall catalyst deactivation. The relative contributions of these two deactivation mechanisms will depend on the fuel composition, to a large degree.

[2] Pritchard, S. C. DiFrancesco, S Kaneko, N. Kobayashi, K. Suyama, and K Iida, "*Optimizing SCR Catalyst Design and Performance for Coal-Fired Boilers*," Presented at EPA/EPRI Joint Symposium on Stationary Combustion NOx Control, May 1995.

Alkali Metals Poisoning

Alkali metals in coal include mainly sodium (Na) and potassium (K). Other alkali metals include lithium (Li), rubidium (Rb), and cesium (Cs). Alkali metals are among the strongest deactivating poisons for SCR catalyst[3]. As with arsenic poisoning, alkali metals react with vanadium blocking the adsorption of NH_3 by the catalyst. In addition, and because alkali metals are water soluble, any moisture condensation can cause the further contamination of the catalyst, aggravating the deactivation of the catalyst. Laboratory studies have demonstrated that the strength of various alkali metals poisons is related to their basicity. For example the effect of K_2O is greater than that of Na_2O. In most coal-fired applications, do to their relatively low concentrations, alkali metals poisoning is not the controlling mechanism of deactivation. However, in certain specialized applications, such as with biomass firing, the relative amounts of alkali metals are much higher, and in these cases alkali metal deactivation may in fact be the primary mode of deactivation.

Alkaline Earth Metals Poisoning

The primary alkaline earth metals of interest to catalyst poisoning are calcium and magnesium. As previously mentioned calcium oxide (CaO) can have either a beneficial or detrimental effect on the catalyst, depending on the quantity of the CaO in the fuel and on the form in which it is found in the flue gas reaching the SCR catalyst. The presence of free CaO in the flue gas has been shown to be of benefit to the catalyst in situations when the fuel contains significant levels of arsenic. As discussed above, limestone is sometimes injected along with coal when the ratio of CaO to arsenic in the ash is too low. Magnesium oxide (MgO) can act as a poison in a manner similar to CaO, although it is relatively rare that MgO poisoning plays a major role in the overall deactivation rate. However, as with sodium and potassium, some specialized fuels, such as biomass, may contain relatively high amounts of magnesium. Thus, the contributing effect of magnesium may be a consideration under certain circumstances.

Calcium-induced deactivation becomes a consideration when the fuel calcium levels become quite high, as is the case when burning PRB coals as discussed previously. The proposed mechanism of CaO-induced deactivation is illustrated in Figure 2-3. The four-step process shows that CaO is first deposited on the catalyst. The particles/molecules are small enough to penetrate into the surface pores, but its deposition does not cause immediate deactivation, as would be the case with a true chemical poison. The second and third steps of the process relate to the diffusion of SO_3 through the bulk gas film and any fly ash that is present on the catalyst surface. It is only after SO_3 diffuses into the pores and reacts with the CaO to form $CaSO_4$ (the fourth step) that actual plugging of the pores occurs. This is because the molecule of $CaSO_4$ is 14%larger (0.338 ml/g versus 0.297 ml/g), which in effect seals the pores reducing the number of effective active sites of the catalysts and limiting the ability of NOx and NH_3 to diffuse into the catalyst and reach active sites, thereby limiting NOx reduction.[4] The SO_3 for the reaction is formed in both the boiler, and across the catalyst. As a result, calcium sulfate deactivation is more noticeable on lower or bottom layers of catalyst, where SO_3 concentrations are higher. Catalyst design, or boiler operation (including higher sulfur fuels), which leads to increased levels of SO_3 will exacerbate calcium-related deactivation.

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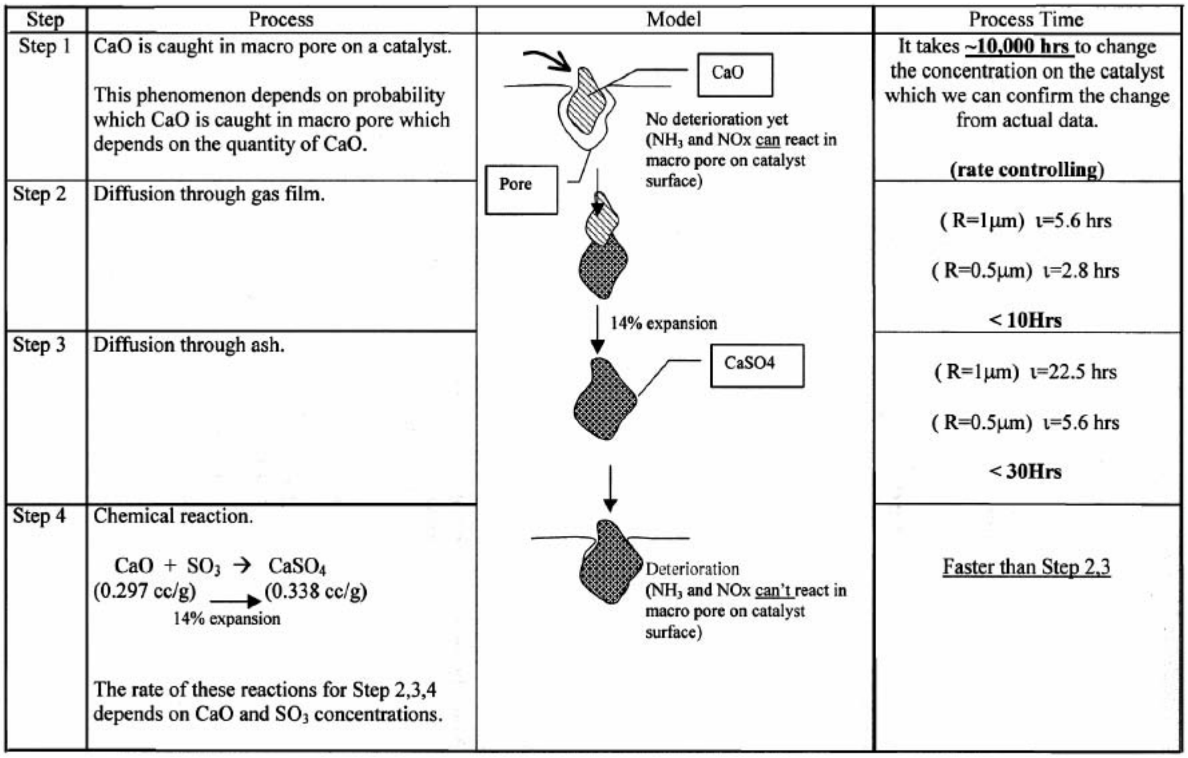
[3] Staudt, J. "*Analysis Of Arsenic In Coal, and The Impact Of Arsenic On Coal Fired Power Plants Equipped With SCR*" Presented at the 2001 EPRI Workshop on Selective Catalytic Reduction, November 2001

[4] Calcium sulfate also expands upon formation, which exacerbates the blockage of pores.

A visual representation of the masking/blocking mechanism is shown in Figure 2-4. This visual representation primarily shows the blocking of macro-pores with $CaSO_4$, but it is important to note that very fine masking layers may be formed on the internal surfaces of the pores themselves. Chemical analyses will show the presence of both calcium and sulfur uptake in the catalyst bulk and on the catalyst surface, such as with XRF analysis. Other analyses, such as with an electron microprobe or via EDX, will show a layer of calcium sulfate on the catalyst surfaces. As mentioned, the $CaSO_4$ masking layer may be quite thin and, as a result, undetectable via physical analyses such as SEM, BET, or mercury porosimetry.



Step	Process	Model	Process Time
Step 1	CaO is caught in macro pore on a catalyst. This phenomenon depends on probability which CaO is caught in macro pore which depends on the quantity of CaO.	CaO Pore No deterioration yet (NH_3 and NOx <u>can</u> react in macro pore on catalyst surface)	It takes **<u>~10,000 hrs</u>** to change the concentration on the catalyst which we can confirm the change from actual data. **(rate controlling)**
Step 2	Diffusion through gas film.	14% expansion	(R=1μm) ι=5.6 hrs (R=0.5μm) ι=2.8 hrs **< 10Hrs**
Step 3	Diffusion through ash.	CaSO4	(R=1μm) ι=22.5 hrs (R=0.5μm) ι=5.6 hrs **< 30Hrs**
Step 4	Chemical reaction. $CaO + SO_3 \rightarrow CaSO_4$ $(0.297\ cc/g) \xrightarrow[\text{14\% expansion}]{} (0.338\ cc/g)$ The rate of these reactions for Step 2,3,4 depends on CaO and SO_3 concentrations.	Deterioration (NH_3 and NOx <u>can't</u> react in macro pore on catalyst surface)	<u>Faster than Step 2,3</u>

Figure 2-3
Arsenic Poisoning Model

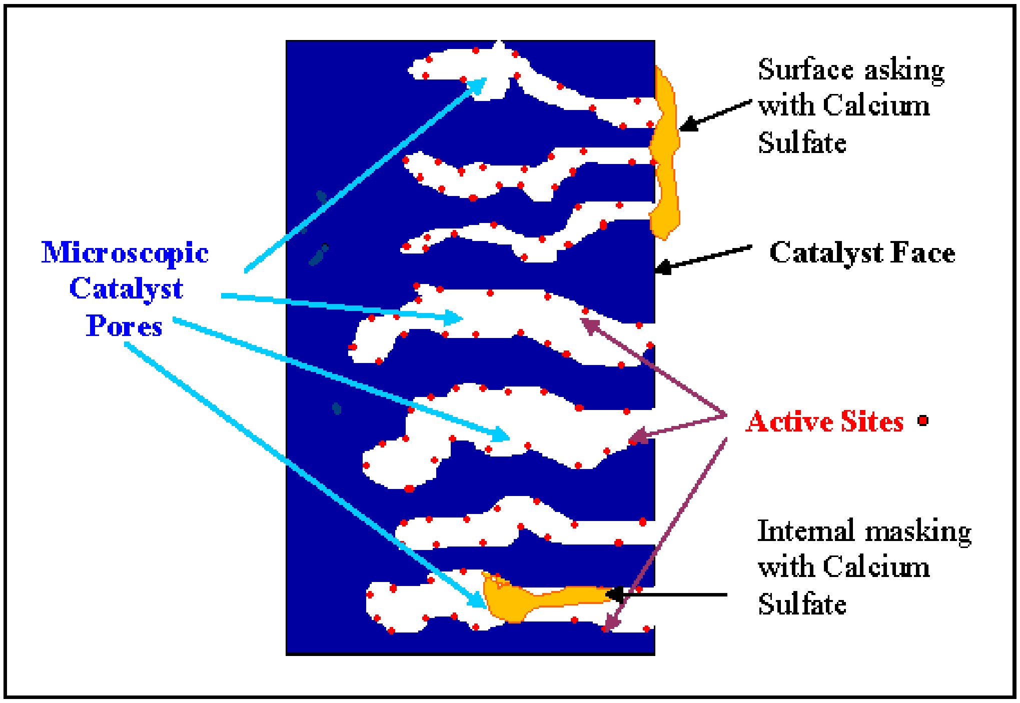


Figure 2-4
Diagram of Calcium Sulfate Masking Mechanism

Catalyst Erosion

Impingement of particulate matter and high interstitial gas velocities erode the catalyst material. Catalysts with hardened leading edges or increased structural strength are less susceptible to erosion. Over time, significant catalyst material may be lost to erosion, resulting in deactivation due to loss of available active sites. Loss of physical integrity is also associated with erosion. The ability of a catalyst to withstand erosion is dependent on the hardness of the ceramic material within the catalyst, the physical construction of the catalyst (plate, honeycomb, etc.), the wall thickness, flue gas velocities, velocity distributions, ash loading, and ash characteristics. In addition, sootblowers may contribute to catalyst erosion if not properly installed and operated. Plate catalyst erosion is shown in Figure 2-5, where leading edge erosion (lower left) is prevalent with bare screen showing, and general catalyst face erosion (lower right) is present where the screen matrix is clearly visible on the entire plate. (It should be noted that depending on the manufacturing technique for plate catalyst, the screen grid-work may be somewhat visible, thus in assessing erosion with any catalyst, it is helpful to compare the potentially eroded catalyst to new catalyst of the same formulation.)

In most cases, erosion is easily detected visually due to entire areas of catalyst being eroded away. However, in other cases uniform wall thinning may have occurred making the presence of erosion less obvious. At present, erosion/attrition catalyst analysis is not included as part of a VGB testing protocol, therefore this information is not available in the database. Catalyst XRF analysis for vanadium (V_2O_5) and molybdenum (MoO_3) could indicate if active metals have been lost due to fly ash attrition, but these would only indicate a loss if the catalyst was non-uniform, i.e., the original catalyst had higher surface concentrations of these species, than did the bulk material.

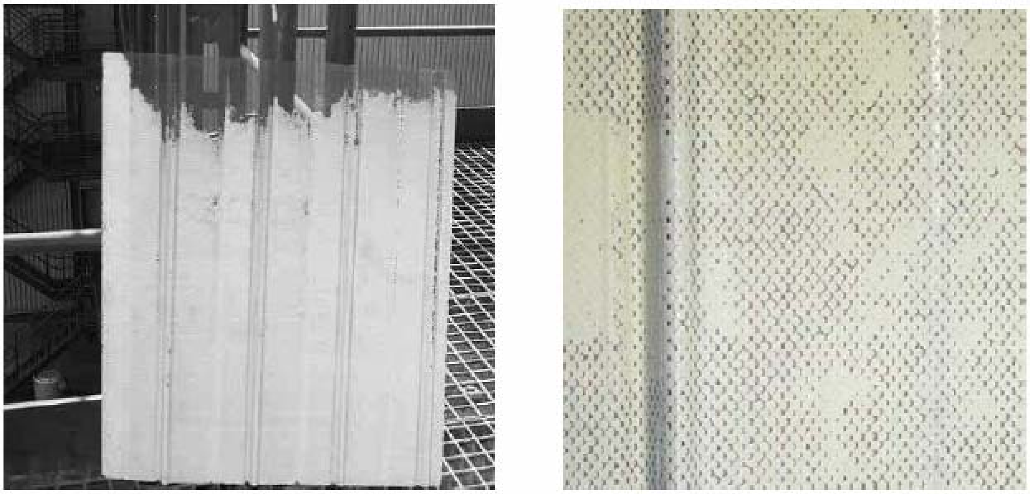


Figure 2-5
Erosion on Plate Type Catalyst

Thermal Sintering

Sintering refers to a change in crystalline structure of the catalyst material and subsequent loss in surface area and altering of the pore size distribution as originally designed. The ceramic structure of SCR catalyst is prone to sintering if temperatures above those for which the catalyst has been designed are encountered. Sintering can cause a permanent loss of catalyst activity due to a change in the pore structure of the catalyst. The amount of thermal sintering and the temperature at which sintering begins to occur depends on the composition and structure of the catalyst. Temperatures widely in excess of the catalyst's design can result in catastrophic deactivation due to the sintering process, which can occur quickly under certain extreme circumstances. Loss of activity due to sintering is irreversible and severe sintering usually results in the need to replace catalyst.

Blinding/Plugging/Fouling

Ammonia-sulfur salts, fly ash, and other particulate matter in the flue gas may cause blinding, plugging, or fouling of the catalyst. The particulate matter deposits on the surface and in the pores of the catalyst. This results in a decrease in the number of sites available for NO_x reduction principally by hindering a gaseous component's access to the site. Heavy external fouling can result in an increase in flue gas pressure drop across the catalyst. These physical deactivation mechanisms often occur slowly, producing a gradual loss in catalyst activity as well as a gradual increase in pressure drop across the catalyst beds. More acute problems may arise if unusual particulate conditions are encountered that may lead to sudden plugging and fouling of the catalyst channels. The presence of large quantities of very large diameter particulate or the presence of "popcorn ash" are examples of acute problems that have been discussed in the industry in the past few years.

3
CATALYST PERFORMANCE TESTING

Introduction

All of the catalyst data presented in this report were obtained using bench-scale testing in accordance with both the VGB and EPRI testing protocols[5]. The VGB guidelines were established in Europe in the mid 80's and served as the basis for the EPRI testing protocol in the United States. The EPRI testing protocol was reviewed by a number of participants including catalyst suppliers, Utility members, and testing laboratories, including the original participants that wrote the VGB guidelines in Europe.

Catalyst testing enables Utilities to know SCR reactor potential, including deNOx performance per layer, as well as SO_2 to SO_3 conversion, and catalyst chemical composition. The following analytical tests are commonly used to evaluate SCR catalysts – basic descriptions have been provided to give the reader a basic understanding of the tests.

DeNOx Activity

Catalyst activity is a measure of the degree to which the catalyst promotes the deNOx reaction. A higher catalyst activity results in a faster reaction rate and theoretically more NOx removal. In practice, the deNOx capability of a catalyst in the field is a function of many variables including catalyst chemical composition, volume, geometry, mass transfer rates, gas temperature, and gas composition. As the catalyst activity decreases with time (termed deactivation), the potential for NOx reduction decreases. In the field, this deactivation results in lower NOx removal, higher ammonia slip levels, or both.

The following equation (Eq. 1) describes the activity of the catalyst (*K)*, with respect to time (*t),* for "normal" deactivation.

$$K = K_o \, e^{(t/\tau)} \qquad \text{(Eq. 1)}$$

Where:
K = catalyst activity at time "t"
t = exposure time
K_o = original catalyst activity
τ = catalyst operating life time constant

More frequently, *relative activity* is utilized as a parameter to express the degree of deactivation that a particular catalyst has experienced. The relative activity is simply the ratio of the activity at some exposure time, represented as K, divided by the original fresh catalyst activity (Ko). Thus a relative activity (K/Ko) of 50% means that the catalyst activity is 50% of that of new.

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[5] *Guideline for the Testing of DeNOx Catalytic Converters, VGB R-302He, 2nd revised version,* published by VGB Kraftwerkstechnik, Klinkestrasse 27-31, 45136 Essen, Germany, 1998, and *Protocol for Laboratory Testing of SCR Catalyst Samples: 2nd Edition,* EPRI, Palo Alto, CA 2007. 1014256.

Figure 3-1 shows an example catalyst deactivation curve based on relative activity (i.e., K/Ko). The shape of this curve is typical of most coal-fired applications, but the absolute values will change significantly depending on the catalyst and the application. As the catalyst activity decreases, the NOx removal efficiency is usually kept constant by injecting more ammonia, thereby increasing the ammonia slip. Note that this deactivation is considered typical, in that it reflects the normal relatively slow deactivation associated with the long-term exposure to catalyst poisons and attrition. Sudden, acute deactivation may occur with other mechanisms, such as severe fouling associated with operational difficulties. When the ammonia slip reaches the maximum design or permitted level (typically 2 ppm), the deNOx level must be reduced or new or reconditioned catalyst must be installed to maintain the original design level of slip. Based upon the original facility design, catalyst replacement or reconditioning will be required at a relative activity level usually in the 60-65% range, corresponding to a life of roughly 16,000-24,000 hours for most installations. (Note that gas-fired installations my achieve lives much longer than those referenced here, due to the limited deactivation that occurs in gas-fired applications.)

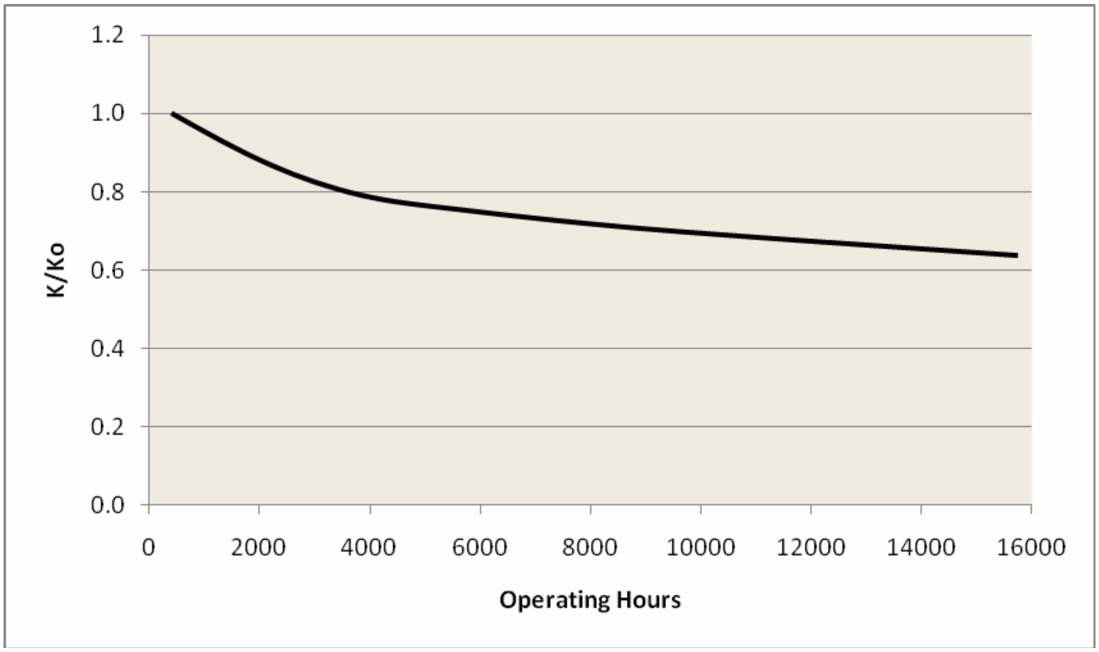

Figure 3-1
Typical Shape of Catalyst Deactivation Curve

Since the same catalyst demonstrates different K-values under different operating conditions, it is crucial that all catalyst bench scale testing be carried out under testing conditions that match the operation of the given unit. These conditions must be consistently used throughout the entire catalyst deactivation tracking program in order to ensure that all data points generated are derived on the same basis. To the degree that the sample actually tested in the laboratory simulates the conditions of the catalyst as a whole in the field, the laboratory measurements will mirror field performance. For example, catalyst which is heavily fouled as present in the field SCR reactor will have an “apparent” low activity, since much of the catalyst may be prevented from participating in the deNOx reaction. However, if cleaned samples of this catalyst are tested in the laboratory, then the sample may indicate a much higher activity than the apparent activity in the field. Thus, the laboratory activity results must be evaluated with a global understanding of the application.

A representative plate sample for bench scale testing is shown in Figure 3-2. The sample is comprised of 12 individual catalyst pates, which are cut into 24 catalyst strips with a width of approximately 145 mm. All 24 catalyst strips are inserted into a sample holder with outer dimensions of 150 mm x 150 mm. Flue gas volumetric flow rate is passes through the channel to representing full-scale conditions.

Figure 3-2
Plate Catalyst Bench Scale Test Module[6]

For bench scale testing related to deNOx activity, the actual measured parameter is NOx reduction efficiency, determined under steady state conditions. Experience has demonstrated that the evaluation of the degree of removal of NOx in terms of a pseudo-first-order rate equation is sufficiently accurate to quantitatively characterize the catalytic activity of the SCR catalyst. The equations that define the activity value K are:

$$K = -Av * \ln(1-\eta_{NOx}) \text{ at } \alpha = 1$$

Where; Av = area velocity [m/h]
ηNOx = NOx removal efficiency
α = NH_3/NOx ratio

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[6] Photo use with permission, courtesy Evonik Energy Services LLC

$$Av = \frac{V}{A_{act}}$$

Where; V = flue gas volume flow rate [m^3/h]
A_{act} = actual physical catalyst surface area [m^2]

$$\eta_{NOx} = \frac{NO_{x\text{-inlet}} - NO_{x\text{-outlet}}}{NO_{x\text{-inlet}}}$$

Where; NOx-inlet = the actual NOx inlet conc. [ppm]
NOx-outlet = the actual NOx outlet conc. [ppm]

In order to cancel out differences in catalyst geometry, such as different plate sizes, plate spacing, pitches, or element lengths, the term catalyst potential (P) defined as P = K/Av is often used. The theoretical minimum catalyst potential (P_{min}) required for the desired deNOx efficiency and permitted ammonia slip can be calculated using a proprietary first order reaction rate exponential equation based on:

- Maximum NOx inlet concentration [ppm]
- Minimum NOx removal efficiency sought [%]
- Maximum acceptable NH_3 slip

SCR performance and catalyst deactivation are generally tracked as potential of each individual layer as well as potential of the entire SCR reactor versus operating time. Each data point generated is entered into the SCR Performance and Catalyst Potential Tracking Sheet.

SO_2 Conversion

The SO_2 conversion rate of the catalyst is becoming more and more of a concern to the utilities, as regulations become increasingly more stringent and as the utilities try to burn higher and higher sulfur coal. The trend toward higher sulfur coal is due to the economics of the lower-priced high sulfur coals, coupled with the ability to remove the resulting SO_2 due to the addition of Flue Gas Desulfurization (FGD) equipment. Since SO_3 formation across the catalyst is directly related to the SO_2 concentration, the trend toward higher-sulfur fuel results in more SO_3 being produced, if catalyst oxidation is not reduced by a commensurate amount. The increased SO_3 concentrations may then lead to acid plume issues. Mitigating these acid plumes has historically been difficult and must be addressed on a case-by-case bias, adding significantly to the cost.

Similar to deNOx activity, SO_2 conversion is routinely measured in the laboratory. Given the difficulty in making field SO_2/SO_3 measurements, this laboratory testing is often the benchmark for SO_2 conversion performance and guarantees. Although SO_2 conversion does not typically change with time to the degree that deNOx activity does, the tracking of SO_2 conversion can provide important information for certain applications where an increase in conversion is possible due to the deposition of certain flue gas constituents which promote SO_2 conversion.

In the bench-scale reactor, the SO_2 to SO_3 conversion rate is measured without ammonia injection. This testing protocol was postulated by VGB-R302He2[7] in order to represent worst case operating conditions, given that the DeNOx reaction competes with SO_2 to SO_3 conversion in the catalyst. As a result, SO_2 to SO_3 conversion usually decreases significantly within the SCR reactor when ammonia is added to the flue gas. Thus measuring SO_2 to SO_3 conversion without ammonia ensures reproducible results and yields the highest "worse case" conversion rate possible. SO_2 to SO_3 conversion is given by Equation 4 below. Note that a sufficient catalyst conditioning time with flue gas without NH_3 is important in order to generate a reproducible value for the SO_2 conversion rate.

$$K_{SO2} = \frac{SO_3\,\text{out} - SO_3\,\text{in}}{SO_2} * 100\ [\%]$$

Where; K_{SO2} =SO_2 conversion rate (%):

SO_3 out: SO_3 outlet concentration (ppmvd)

SO_3 in: SO_3 inlet concentration (ppmvd)

SO_2: SO_2 flue gas concentration (ppmvd)

X-Ray Fluorescence

X-Ray Fluorescence (XRF) is a routine analytical technique currently used by most laboratories analyzing SCR catalysts. This technique gives bulk or surface chemical composition (depending on the sample preparation) of a large number of analytes. To estimate the influence of intruding elements such as arsenic, soluble and mobile alkali salts and phosphorus on the chemical composition of the catalyst's bulk material, parts of the catalyst sample are ground to a fine powder for analysis. Changes of the bulk chemistry are characteristic for the long-term intrusion rate of gaseous and soluble liquid catalyst poisons.

Identifying masking and plugging effects on the catalyst surface is important in order to characterize possible formations of surface layers or pore blocking. Flat parts of the catalyst surface exposed to the flue gas are analyzed without further sample preparation. Differences between bulk and surface analysis are critical for assessing the experienced deactivation rate as well as the deactivation mechanisms involved.

Chemical analysis was performed for catalyst samples taken from the flue gas inlet and outlet sides of all catalyst samples separately in order to determine flue gas flow directional and layer dependent deactivation effects. Flue gas flow conditions in the catalyst channels change from turbulent to laminar within the first approximately 4" (~100 mm). Therefore, the first 4" – 6" (100 – 150 mm) of the catalyst's flue gas inlet section is very sensitive in rapidly detecting absolute chemical composition changes. The catalyst's flue gas outlet side is more representative for the long-term quantitative effect of the overall chemical composition changes observed during catalyst operation. To correlate the activity loss with chemical impacts, so called

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[7] Guideline For The Testing Of DeNOx Catalytic Converters, VGB R-302He, 2nd revised version, published by VGB Kraftwerkstechnik, Klinkestrasse 27-31, 45136 Essen, Germany, 1998.

weighted average values for the respective chemical elements are commonly used. Based on Evonik's long-term SCR operating, testing and analysis experience the best results are obtained for each compound with a weighted average of 20% of the inlet side value and 80 % of the outlet side value. Such weighted average values are presented in all subsequent graphs.

Bench-Scale Test Facility

Bench-scale reactors in accordance with VGB-R302He are designed specifically for the sole purpose of evaluating SCR catalyst under simulated, controlled plant conditions. It provides the only practical way of examining SCR DeNOx catalyst in a non-destructive manner while generating absolute values for catalyst activity, SO_2/SO_3 conversion rate and pressure drop. The most important feature of a bench scale reactor is its particular suitability for exactly replicating the actual operating conditions of a full scale SCR reactor while still ensuring useful data. The only two deviations from the actual operation conditions of the full scale SCR reactor are the lack of any fly ash in the bench scale and the molar ratio of ammonia to NOx, which is commonly referred to as set equal to 1.

Since the presence or absence of fly ash in the flue gas has no influence on the actual activity of the catalyst, it is more practical and less interfering to operate a bench scale reactor without fly ash in the flue gas. It is neither feasible to test several catalyst samples in series nor to test at the same molar ratio of NH_3 to NOx as present at the inlet of the full scale SCR reactor, since the underlying math as outlined below no longer applies under such different conditions. Also, as the availability of NH_3 is the limiting factor of the DeNOx reaction in a full scale SCR system, which is not desired in a bench scale test for determining the catalyst's activity, the molar ratio of NH_3 to NOx must be set to 1. However, to enable correct measurements of the catalytic activity (K) and the SO_2/SO_3 conversion rate under the exact same conditions that the catalyst experiences in an actual utility SCR system, catalyst samples must be exposed to synthetic flue gas of the exact same composition, velocity and temperature as present in the full-scale system.

It is of critical importance for the validity the data obtained that the operating conditions of the bench scale reactor during catalyst performance testing replicate the actual SCR operating conditions of the full-scale plant as closely as possible. This includes particularly the same actual linear flue gas velocity, area velocity, temperature, O_2 content, NOx content, SO_2 content, and SO_3 content. The moisture content, which cannot be adjusted exactly to full-scale operating conditions as a result of the synthetic flue gas generated by burning a mixture of propane and butane, also affects the catalytic activity. All determined activity values are adjusted for the difference between the actual operating moisture content of the flue gas in the full-scale SCR and the flue gas moisture content during bench scale testing. Evonik's bench-scale test facility is shown in Figure 3-3.

Figure 3-3
Evonik's Bench Scale Test Facility[8]

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[8] Photo use with permission, courtesy Evonik Energy Services LLC

4

DATABASE ANALYSIS

Introduction

Several case studies based upon the database analysis are presented below, divided by fuel type. These include; 1) PRB Coal applications, 2) Illinois Basin Coal applications, and 3) Eastern Bituminous Coal applications. In addition to these case studies, a correlation analysis reflecting the relationship between catalyst sample arsenic level and deactivation rate is presented.

Impacts of PRB Fuel on Catalyst Deactivation

Exposure and Test Conditions

The deactivation of a particular catalyst is governed by a number of parameters, including flue gas composition and SCR operating conditions, but most important is the fuel and ash constituents. This section presents a catalyst deactivation case study using information from a unit burning 100% PRB fuel. SCR operating conditions are summarized on Table 4-1. The unit is a hot side SCR and is filled with four layers of plate type catalyst. Additional information can be found in Appendix A, which includes data for this case study, as well as other similar applications.

Table 4-1
SCR Operating Conditions

Plant Name	R
Fuel Type	PRB
Catalyst Type	Plate
Unit/SCR ID #	1
Cleaning System	Sootblowers
SCR By-pass	yes
High/Low Dust	High
Cycling Unit (Yes/No)	no
Installed Number of Layers	4
Layer % plugged (LPA & ash)	10

During catalyst testing, flue gas conditions, presented in Table 4-2, were consistently used throughout the test program in order to ensure that all data points generated were derived on the same basis.

Table 4-2
Flue Gas Test Conditions

Test Conditions	
Flue Gas Temperature (^oF)	693
Linear Velocity (act. m/s)	2.3
Area Velocity (m/h)	40.4
Inlet NO (ppmvd)	346
Inlet SO_2 (ppmvd)	206
O_2 (% dry)	3.2
H_2O (%)	12

Fuel ash composition is provided in Table 4-3. CaO represented 26.5% of the bulk ash composition, while P_2O_5 accounted for 0.95%.

Table 4-3
Ash Composition

Ash Composition - 100% PRB Fuel	
SiO_2	28.97
Al_2O_3	12.88
TiO_2	1.03
Fe_2O_3	4.6
CaO	26.5
MgO	5.09
K_2O	0.55
Na_2O	1.68
SO_3	12.3
P_2O_5	0.95
SrO	0.26
BaO	0.55
MnO_2	0.03

Deactivation Rate

SCR catalyst deactivation rates after 7,100 hours and 50,700 hours are presented in Figure 4-1. As noted, both layers appear to be deactivating at similar rates, averaging 23 m/h (K/Ko = 50%) at the 7,100 hour data point. The designed guaranteed life for this particular catalyst was 65% after 16,000 hours. As the exposure hours increased to 50,400, the decline in activity was not as great as with the initial exposure period, resulting in a final activity averaging 16.6 m/h (K/Ko = 36%). The original SO_2 to SO_3 conversion rate was 0.3%, and was not reported after the initial measurement.

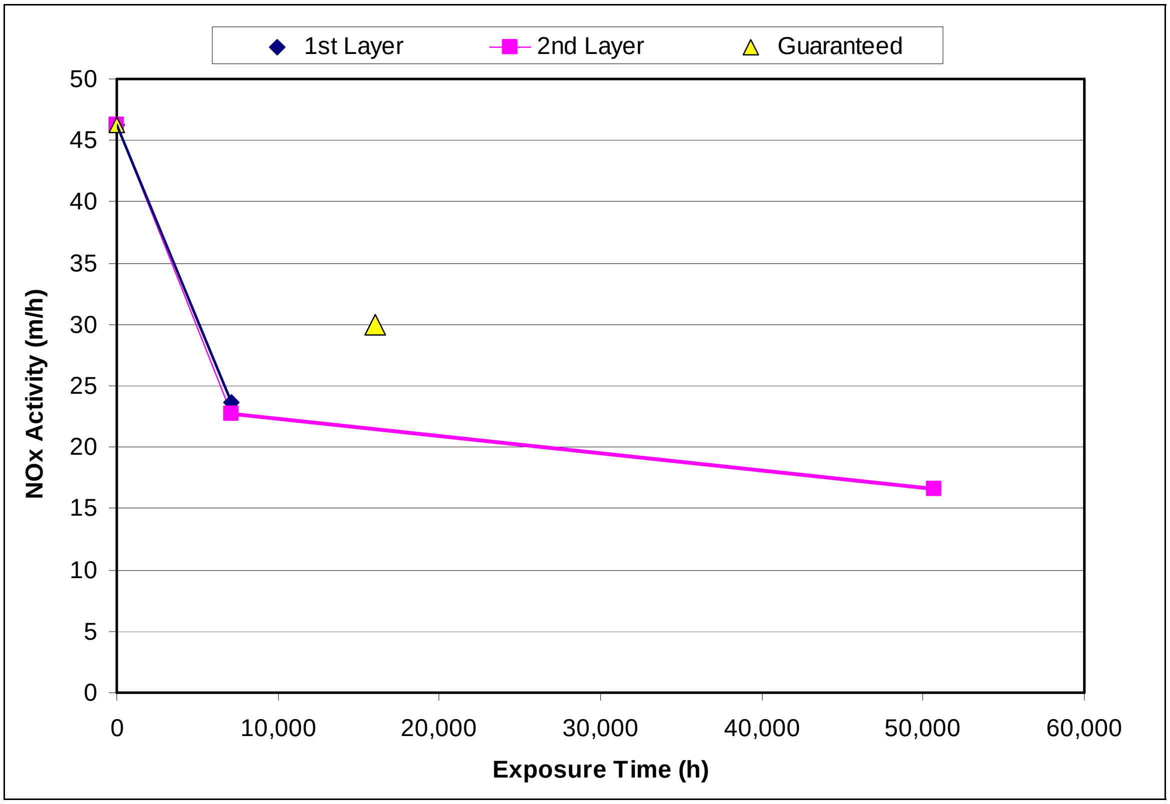

Figure 4-1
SCR Catalyst Deactivation Rates

Chemical Analysis Data

Catalyst samples were analyzed using XRF. These analyses lead to number of conclusions. Due to the better mass transfer in the turbulent flue gas inlet section of the catalyst layers, higher concentrations of contaminants were found in that region compared to the outlet section as expected. This higher contamination level compared to lower catalyst levels is also the result of the flue gas becoming depleted in the contaminants, at least until upper catalyst layers become saturated or completely masked. This effect is illustrated in Figure 4-2, where P_2O_5 saturated in the bulk of the catalyst in both layers at 3.5%. Surface P_2O_5 in the first and second layers was 24% and 19% respectively (based upon the 7,100 hour data, using an average for the second layer).

Additional surface data are shown in Figure 4-3, which compares the levels of various analytes as a function of exposure time. Interestingly, the data indicate that there was not any appreciable additional uptake of contaminants with aging past the 7,100 hour exposure time. This finding also held true for the bulk data.

Calcium and sulfur were both noted in the XRF analysis, presumably indicating the deposition of calcium sulfate, although it should be noted that XRF results does not distinguish the actual compound. Given the exceptionally high levels of phosphorus, however, one might conclude that phosphorus poisoning was the controlling mechanism of deactivation, with contributions from calcium sulfate masking, as well as poisoning by magnesium, sodium, and potassium. In fact, phosphorus poisoning of catalyst installed in units firing PRB fuel is a well known problem and typically combined with surface blinding becomes the main deactivation cause. Unfortunately, and contrary to arsenic poisoning, there is no known way of mitigating phosphorus poisoning. However, just like arsenic, phosphorus could potentially be removed during catalyst reconditioning.

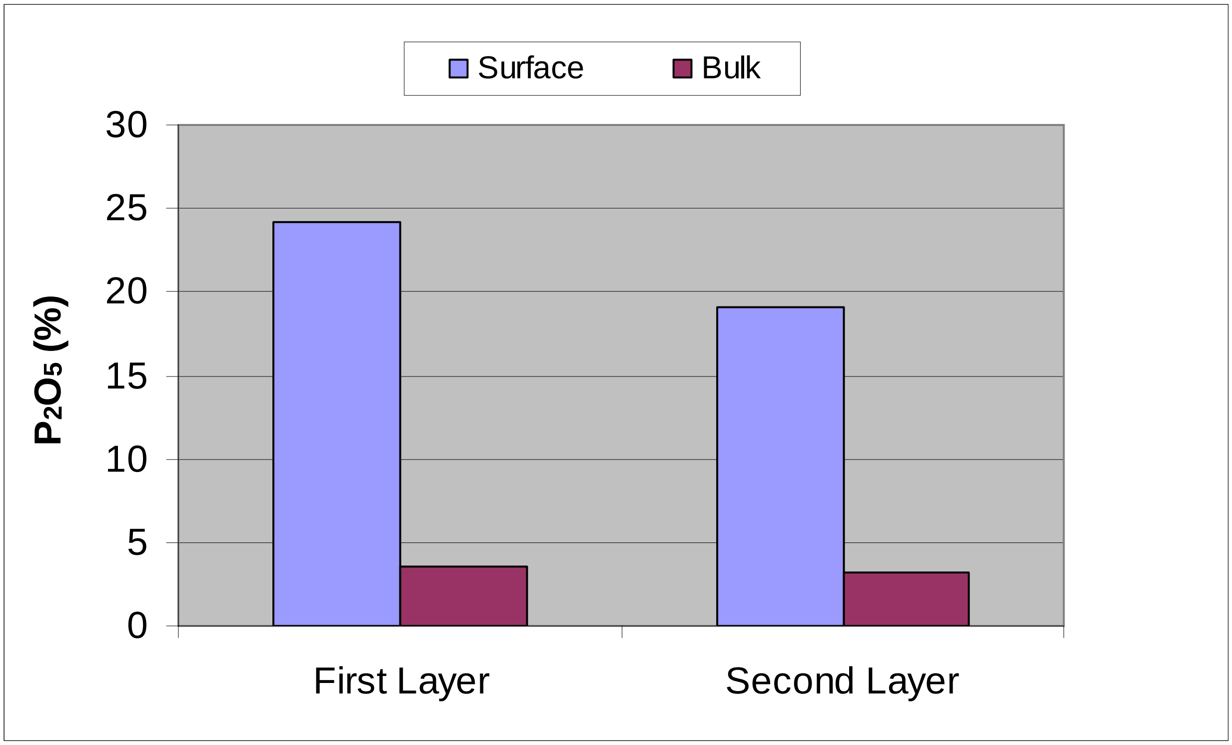

Figure 4-2
SCR Catalyst P_2O_5 Surface and Bulk Concentrations

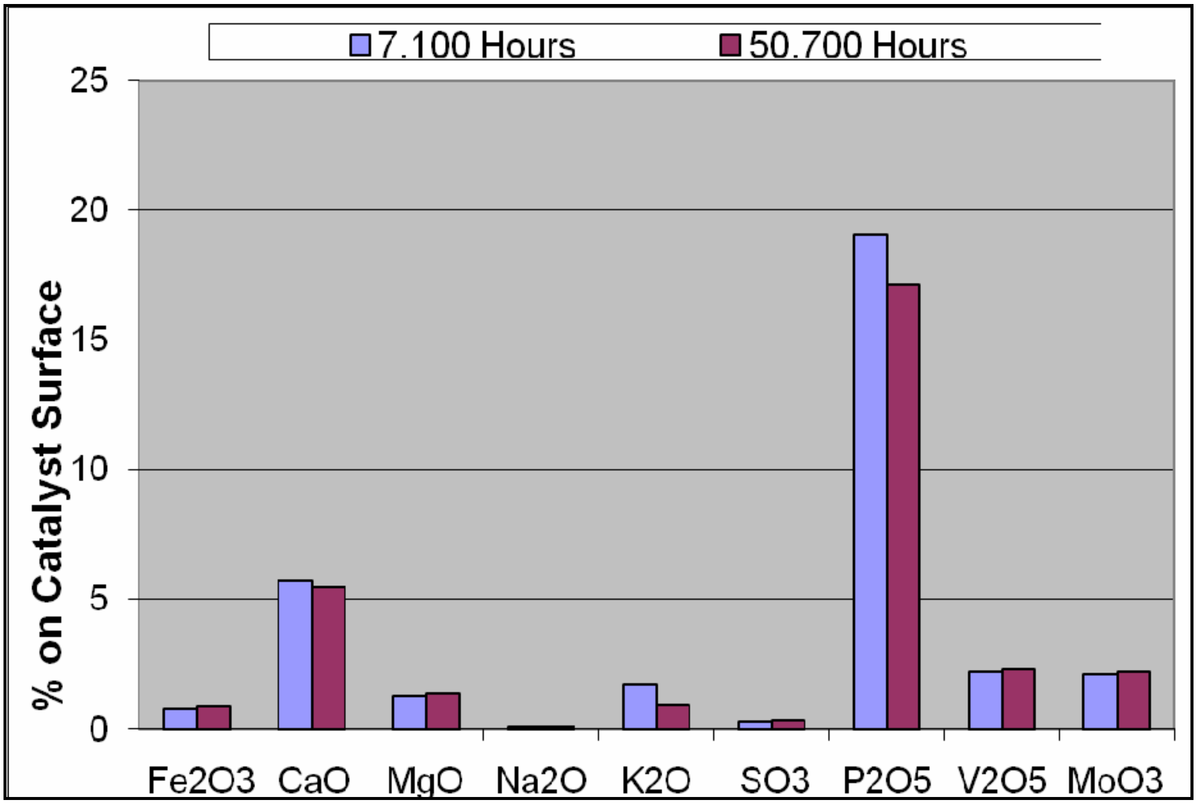

Figure 4-3
SCR Catalyst P_2O_5 Surface Concentrations – Second Layer

Figure 4-4 shows comparative data for the surface and bulk measurements. Surface enrichment was noted with calcium, magnesium, and especially phosphorus, as previously discussed. Vanadium also showed surface enrichment, which may be due to the catalyst manufacturing process, or due to deposition of vanadium compounds originating in the fuel. Although not shown on this plot, there was a slight reduction in titania on the surface analysis as compared to the bulk. This is not an unusual occurrence, since the surface deposition of various compounds leads to a “dilution” effect resulting in an apparent lower level of titania. This should not be taken to mean that the titania is actually removed from the surface.

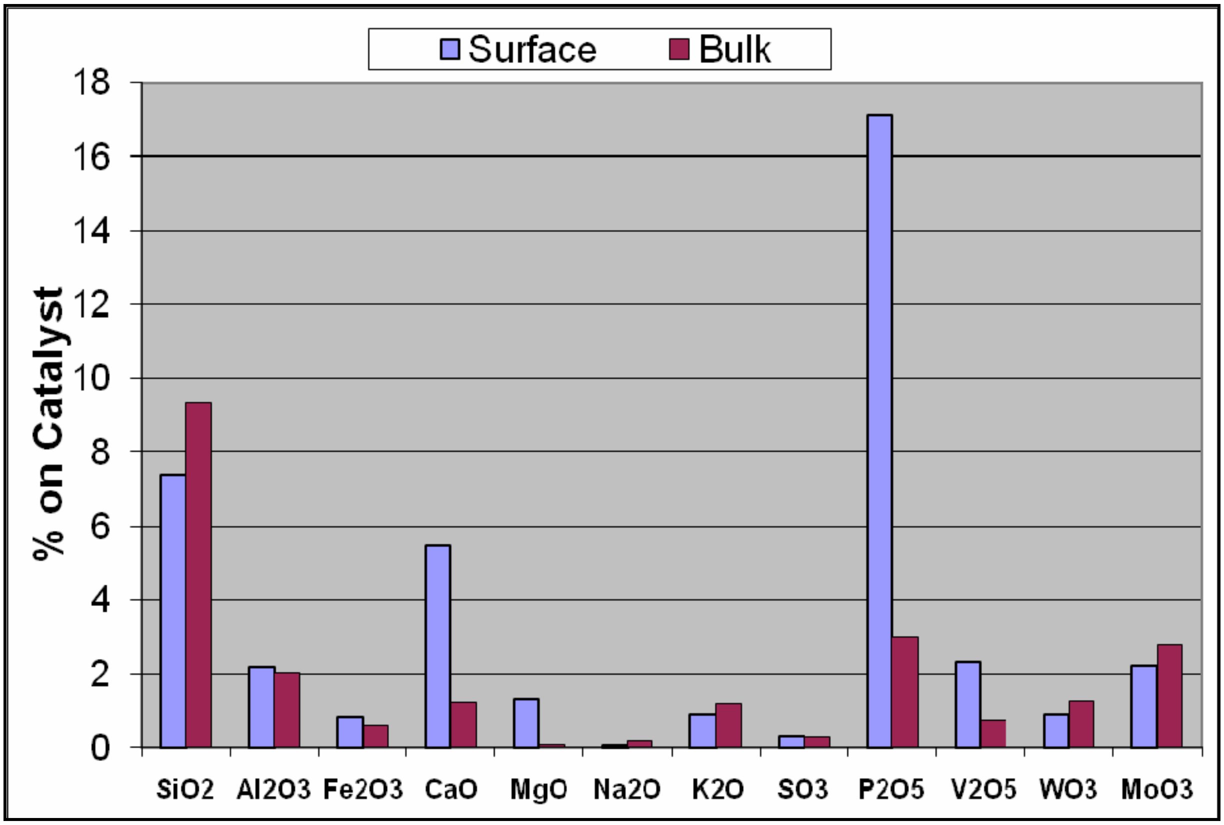

Figure 4-4
Comparative Surface and Bulk Concentrations

Impacts of Southern Illinois Fuel on Catalyst Deactivation

Exposure and Test Conditions

This case study provides an example for a unit burning a Southern Illinois Bituminous fuel. The SCR was filled with plate type catalyst and was operated at the conditions listed in Table 4-4. After 10,871 hours in service, catalyst samples were removed and tested for NOx activity, SO_2 to SO_3 conversion, and XRF chemical composition, all in accordance with the VGB guidelines. Flue gas conditions used during testing are listed in Table 4-5. Additional data for this case study can be found in Appendix B, along with data for other similar applications.

Fuel ash characteristics are shown on Table 4-6. Arsenic in the fuel was estimated at 10 ppm. It should also be noted that arsenic in bituminous fuel can range between very low ppm concentrations up to roughly 70 ppm. Thus, this particular fuel could be considered a mid arsenic fuel. As previously indicated, calcium (CaO) acts as a scavenger for free arsenic in flue gas. Thus the arsenic to calcium ratio dictates the catalyst deactivation rate. In this case, CaO concentration in the fly ash was 1.8%.

Table 4-4
SCR Operating Conditions

Plant Name	Q
Fuel Type	Bituminous
Catalyst Type	Plate
Unit/SCR ID #	1
Cleaning System	Sootblowers
SCR By-pass	yes
High/Low Dust	High
Cycling Unit (Yes/No)	no
Installed Number of Layers	3
Layer % plugged (LPA & ash)	10

Table 4-5
Flue Gas Test Conditions

Test Conditions	
Flue Gas Temperature (^oF)	725
Linear Velocity (act. m/s)	8.52
Area Velocity (m/h)	29.85
Inlet NO (ppmvd)	250
Inlet SO_2 (ppmvd)	1050
O_2 (% dry)	3.5
H_2O (%)	11

Table 4-6
Ash Composition

Ash Composition	
SiO_2	52.51
Al_2O_3	20.62
TiO_2	0.97
Fe_2O_3	14.41
CaO	1.8
MgO	0.96
K_2O	2.12
Na_2O	0.69
SO_3	2.85
P_2O_5	0.43
SrO	0.09
BaO	0.07
MnO_2	0.03
Fuel Arsenic to Ash CaO ratio	5.00

Deactivation Rate

SCR catalyst deactivation rates for the first and second layers are summarized in Figure 4-5. Vendor guarantees were K/Ko of 60% after 16,000. The data indicated that the second layer was deactivating as predicted (K/Ko = 75% after 10,800 hours), while the first layer was deactivating at a faster rate (K/Ko = 69% after 10,800 hours).

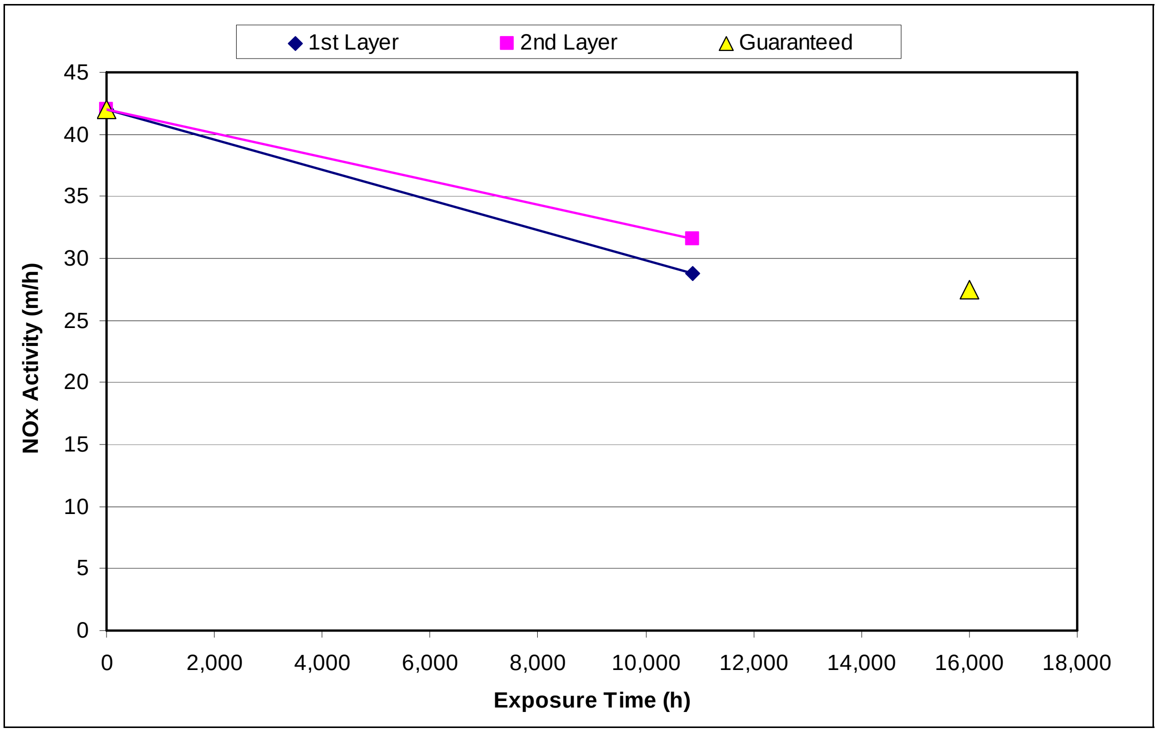

Figure 4-5
SCR Catalyst Deactivation Rates

Chemical Analysis Data

Arsenic uptake in the catalyst is presented in graphical form in Figure 4-6. As opposed to P_2O_5 deactivation presented in the previous case study, arsenic attacks both the surface as well as the bulk of the catalyst. Overall, arsenic concentration levels are higher in the top layer, consistent with the faster deactivation rates. Arsenic concentrations on the top catalyst surface were 11,728 ppmw, compared to 10,800 ppmw in the second layer. Similarly, arsenic concentrations in the bulk of the top catalyst layer were 14,000 ppmw, compared to 7,561 ppmw in the second layer.

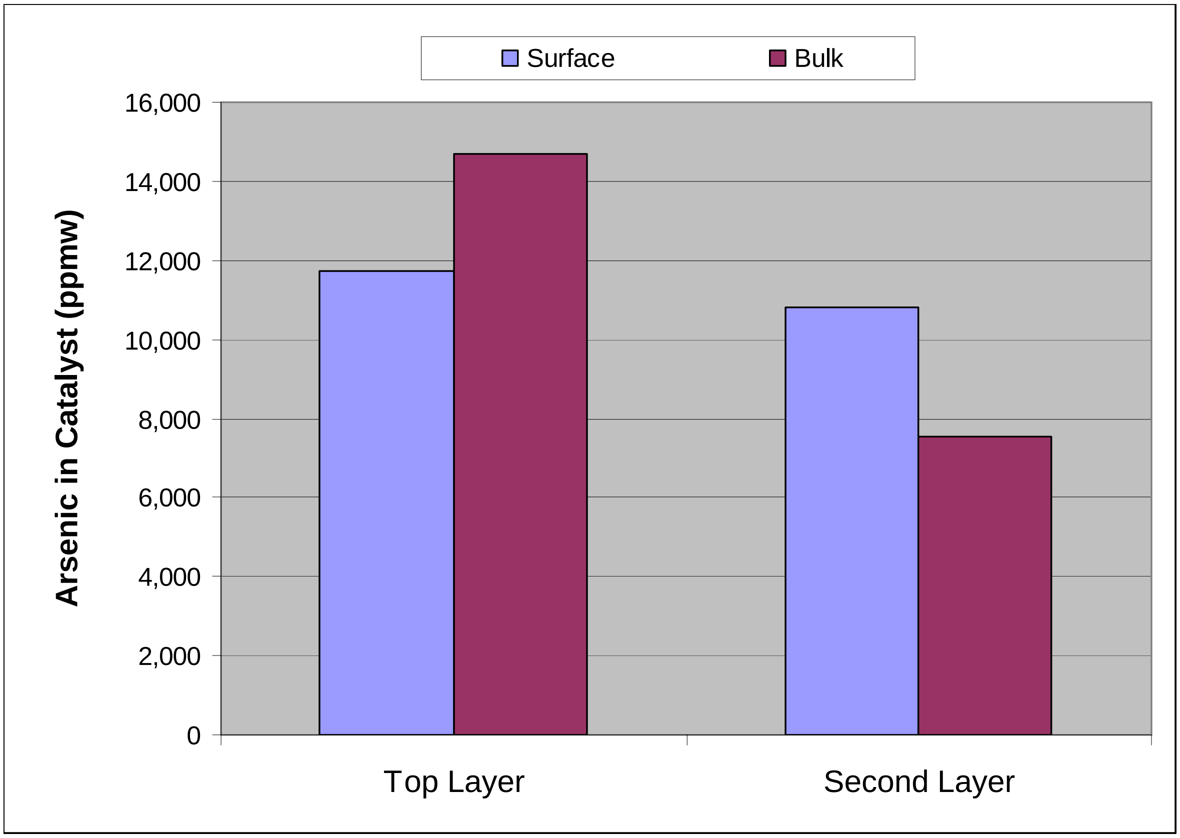

Figure 4-6
SCR Catalyst Arsenic Surface and Bulk Concentrations

Figure 4-7 shows comparative data for the first and second catalyst layer, based upon the surface data. The data show significant amounts of both SiO_2 and Al_2O_3 which are primary ash constituents. These two components are actually higher on the second layer than on the first, perhaps due to the particular portion of catalyst that was sampled having a higher ash loading. Phosphorus is also higher on the second layer sample, than on the first. The exact reasons for this are unknown, but non-representative sampling may play a role. Note that aluminum and silicon may also be present on the catalyst as silicate glass fibers, which are incorporated into the TiO_2 bulk material to reinforce the mechanical strength of the catalytic ceramic mass. Reductions in vanadium and molybdenum between the first and second layer sample may simple be due to the "dilution" effect mentioned above, where the presence of substantial ash constituents results in an apparent dilution of these catalytic species. Overall, the data indicate that arsenic is the primary cause of deactivation, with a possibility that phosphorus is contributing. Unlike the previous case, the calcium and SO_3 levels are quite low, consistent with the application to bituminous fuels.

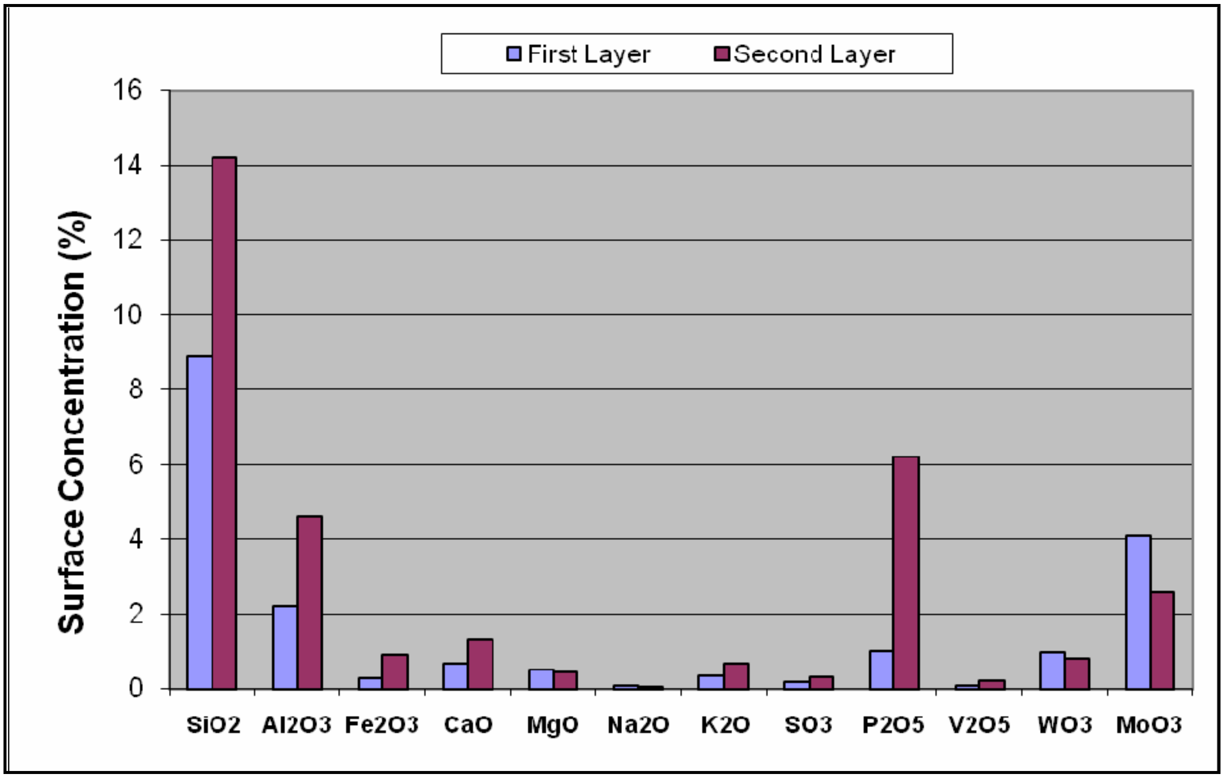

Figure 4-7
Comparative First and Second Layer Surface Composition Data

Figure 4-8 shows comparative data for surface versus bulk analysis. The levels of almost all constituents shown are similar between the surfaces and bulk analyses, with only a slight surface enrichment of silicon, the primary ash constituent being noted. The phosphorus was actually higher in the bulk than on the surface, indicating that phosphorus had penetrated the catalyst bulk. This tends to indicate that phosphorus was acting as a poison rather than simply as a surface constituent associated with the ash.

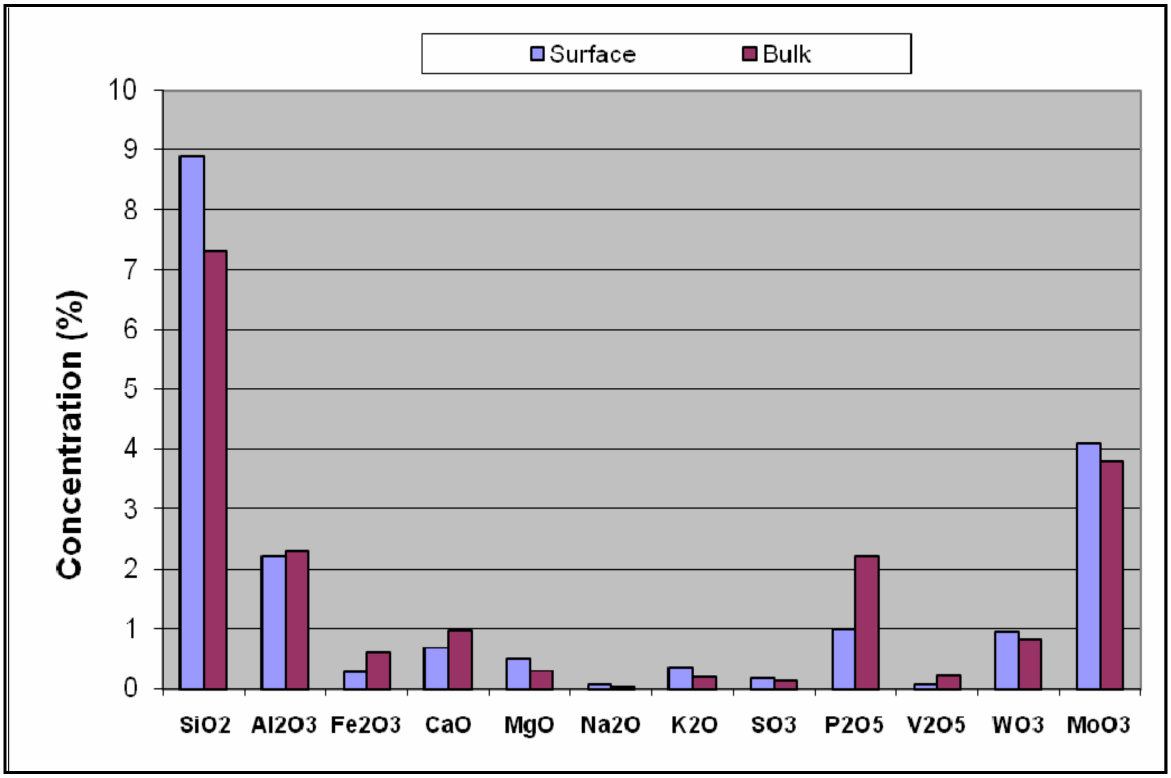

Figure 4-8
Comparative Surface and Bulk Composition Data

Impacts of Eastern Bituminous Fuel on Deactivation

Exposure and Test Conditions

This case study presents tests results for catalyst deactivated on Easter Bituminous fuel. SCR operating conditions are listed on Table 4-7; the system was filled with three layers of plate type catalyst and operated at nominally 650^{o}F. After 17,000 hours in service, plates were removed and tested for NOx activity, SO_2 to SO_3 conversion, and chemical composition. Flue gas test conditions are summarized in Table 4-8. Appendix C contains additional detailed information for this case study, along with data for other similar applications.

Table 4-7
SCR Operating Conditions

Plant Name	M
Fuel Type	Bituminous
Catalyst Type	Plate
Unit/SCR ID #	3/Layer 1
Cleaning System	Sonic Horns
SCR By-pass	Yes
High/Low Dust	High
Cycling Unit (Yes/No)	No
Installed Number of Layers	3
Layer % plugged (LPA & ash)	15

Table 4-8
Catalyst Test Conditions

Test Conditions	
Flue Gas Temperature (^{o}F)	651
Linear Velocity (act. m/s)	5.71
Area Velocity (m/h)	31.9
Inlet NO (ppmvd)	250
Inlet SO_2 (ppmvd)	2000
O_2 (% dry)	3.5
H_2O (%)	8

The host unit burned a mid arsenic fuel (10 ppm). However, as opposed to the previous case study, this fuel has a relatively higher level of calcium (4.3%) which improved the removal of gaseous arsenic. This fuel seems to be the most catalyst friendly and gave more longevity, since the fuel doesn’t have an unbalanced arsenic to calcium oxide ratio.

Table 4-9
Ash Composition

Ash Composition	
SiO_2	46.48
Al_2O_3	18.87
TiO_2	0.95
Fe_2O_3	21.562
CaO	4.294
MgO	0.908
K_2O	2.557
Na_2O	0.4985
SO_3	3.706
P_2O_5	0.19
SrO	0.0309
BaO	0.064
MnO_2	0.0416
Fuel Arsenic to Ash CaO ratio	2.30

Deactivation

The progression of the catalyst deactivation is summarized below in Figure 4-9, which shows the loss in activity after 17,000 hours in service. Deactivation rates on the first and second catalyst layers were 83% and 80% respectively. The guaranteed life for this particular catalyst was 20,000 hours. It is clear from Figure 4-9 that the actual rate of deactivation is well below the expected deactivation rate.

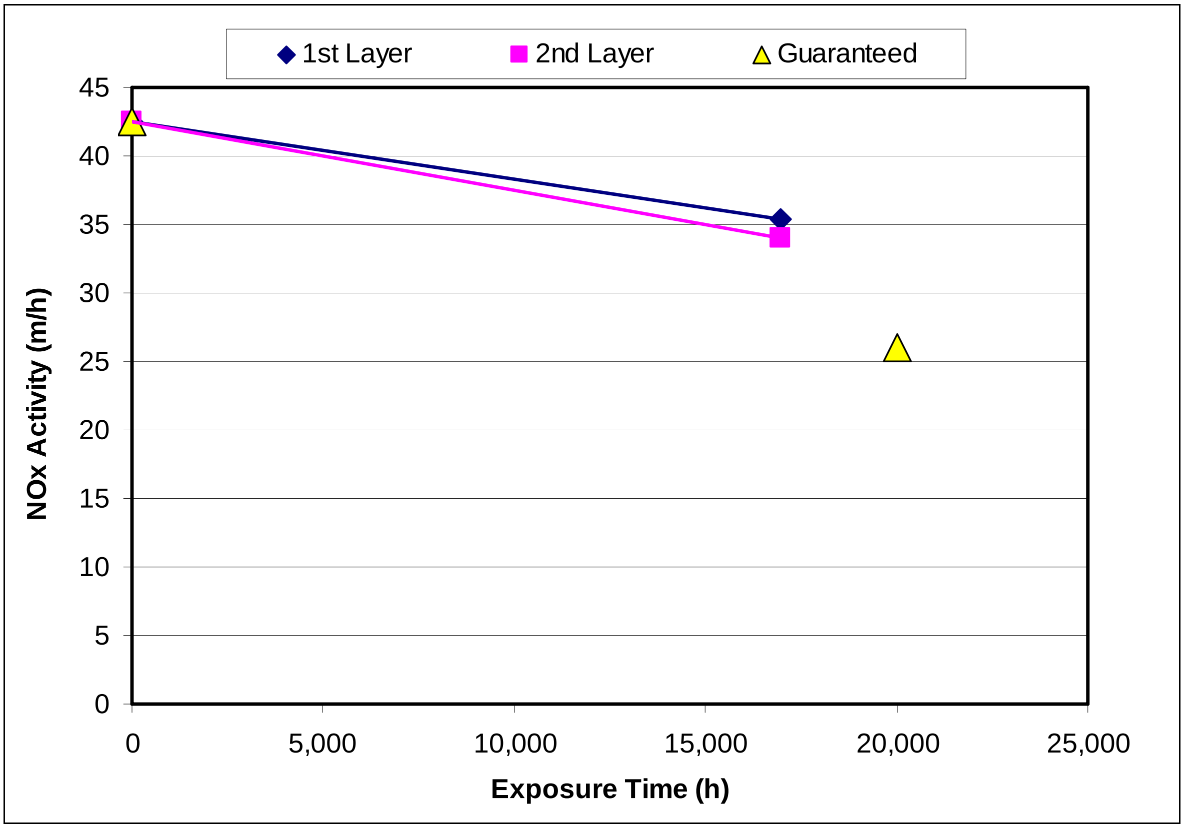

Figure 4-9
SCR Catalyst Deactivation Rates

Chemical Analysis Data

Figure 4-10 shows the arsenic uptake per catalyst layer (based on surface measurements – bulk data were not available). As expected, the first layer has adsorbed higher arsenic concentrations compared to the second layer. However, arsenic concentrations are relatively low in both layers, even after 17,000 hours in service. This example presents the importance of CaO in fuel in mitigating arsenic.

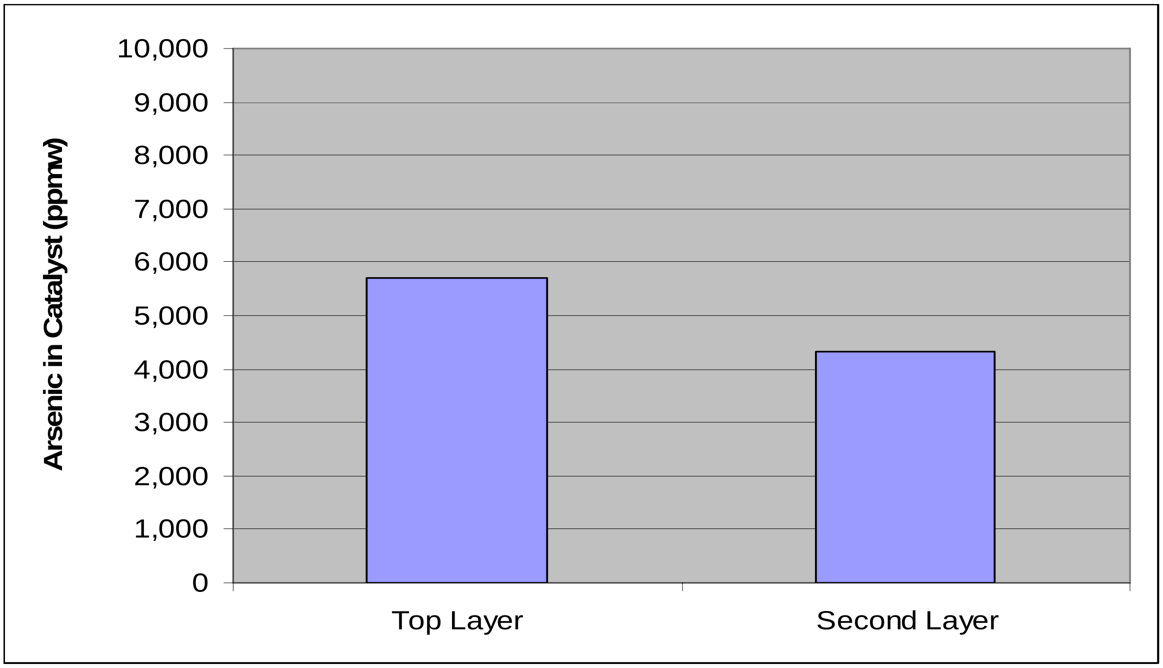

Figure 4-10
SCR Catalyst Arsenic Surface Concentrations

Figure 4-11 shows comparative data for the first and second layer samples (based on surface data). These data show the typical expected ash constituents, such as silicon, aluminum, iron and calcium. As noted above, the calcium level in the fuel was higher than in the previous case study, and as one would expect the calcium concentration on the catalyst is higher. There is very little change in concentration of the constituents between the layers. Given the low arsenic levels on the catalyst, coupled with low levels of other poisons, such as magnesium, sodium, potassium, and phosphorus, it is not surprising that he catalyst activity has not deteriorated to any large degree over the relatively long catalyst exposure life.

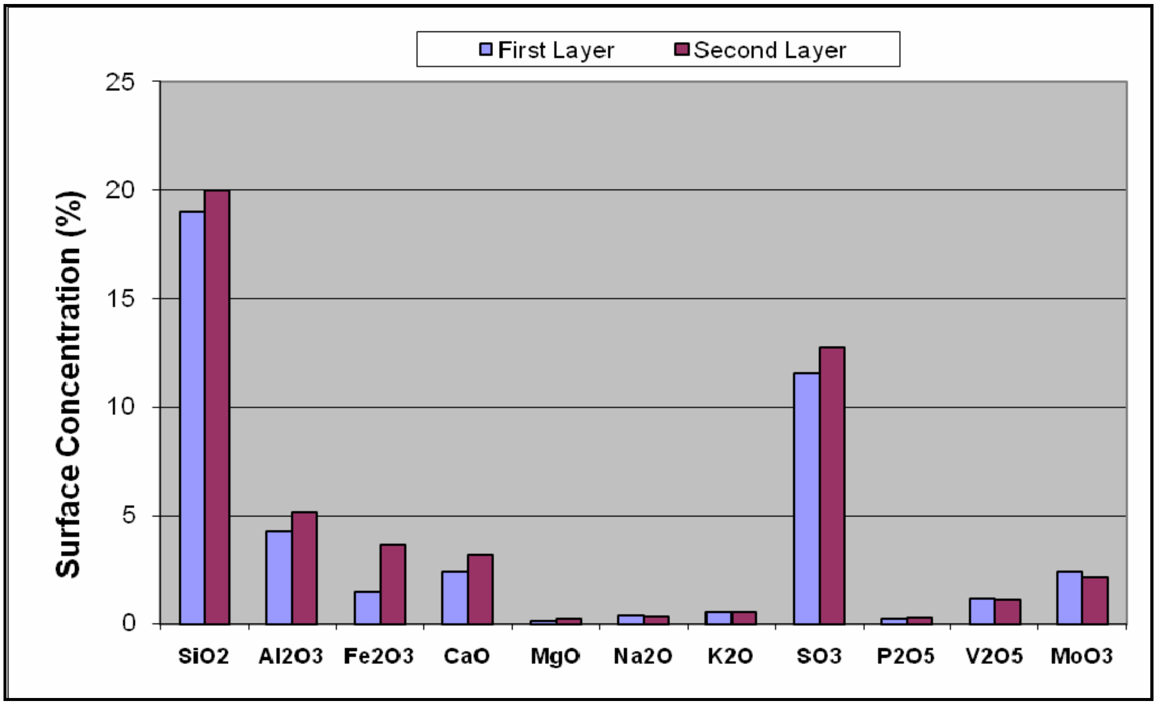

Figure 4-11
Comparative First and Second Catalyst Layer Samples

Figure 4-12 shows comparative data for the surface and bulk chemical analyses (based on the first catalyst layer data). These data show some surface enrichment in common fly ash species, such as silicon, iron, and calcium. Aluminum, a primary ash species, did not show the same surface enrichment, which appears to be a data anomaly. In particular, SO_3 showed strong surface enrichment, possibly indicating the presence of sulfates on the catalyst surface, possibly as calcium sulfate to some degree. As above, typical catalyst poisons such as magnesium, sodium, potassium, and phosphorus were quite low in all measurements.

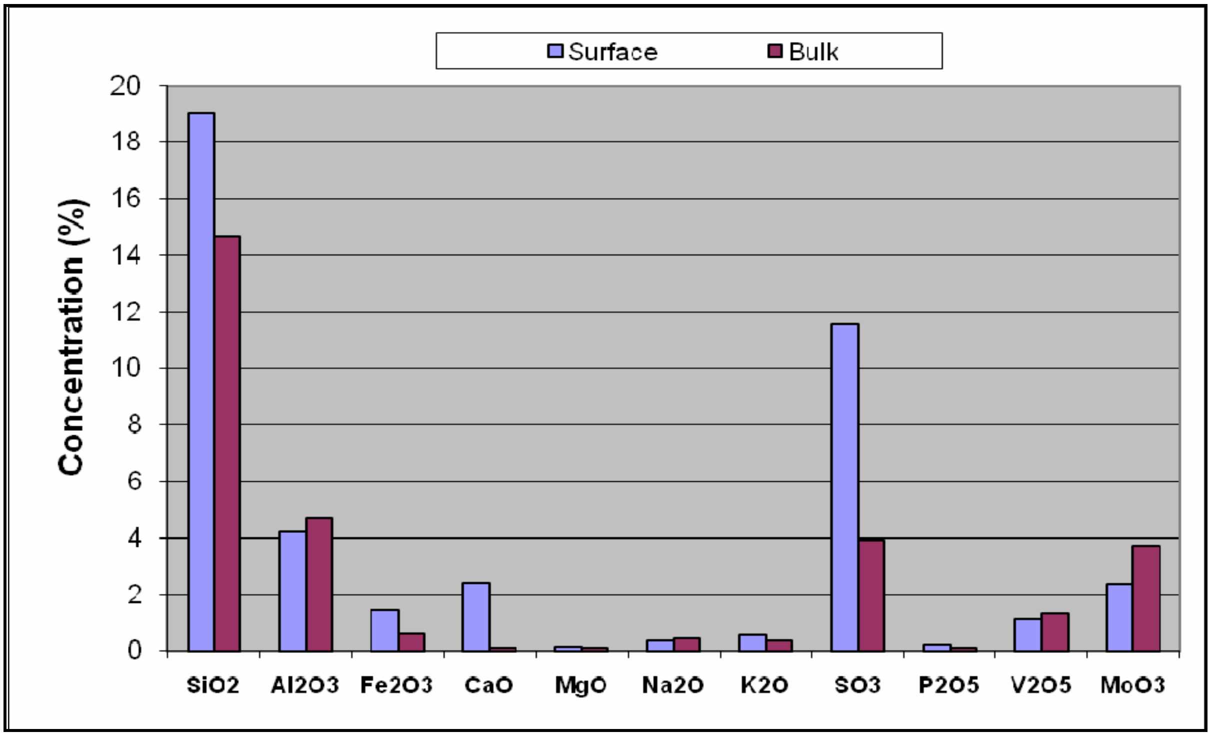

Figure 4-12
Comparative Surface and Bulk Data

Correlation of Catalyst Arsenic Level to Deactivation Rate

As discussed, arsenic poisoning is the primary mode of catalyst deactivation for bituminous fuels. The following data correlates arsenic content on plate-type catalyst to deactivation. The analysis includes a total of 12 catalyst samples; all removed from the first (top) layer and from different SCR reactors. Catalyst information and test results are presented in Appendix C.

Figure 4-13 and Figure 4-14 present arsenic concentrations in the catalyst surface and bulk respectively. Typically a catalyst reaches the end of its life when activity reaches between 65% and 60%, depending on catalyst make. Based on these data, plate type catalyst will reach the end of its life when catalyst arsenic concentrations approximate 18,000 to 22,000 ppmw. The arsenic deposition rate will vary according to application. For instance, one sample accumulated 5,700 ppmw after 17,000 hours of exposure time, while another sample adsorbed 18,000 ppmw after 11,000 hours. It is expected that the arsenic deposition rate will primarily be a function of gaseous arsenic and calcium concentration in the flue gas.

Deactivation modes other than arsenic poisoning may participate in catalyst deactivation associated with eastern bituminous fuels. However, no adverse trends were found in the data linking Na_2O, K_2O, or P_2O_5 to catalyst deactivation. Note that for the data set, Na_2O concentrations ranged between 0.19% and 0.57%, K_2O concentrations ranged between 0.13% and 0.56%, and P_2O_5 ranged between 0.12% and 0.94%.

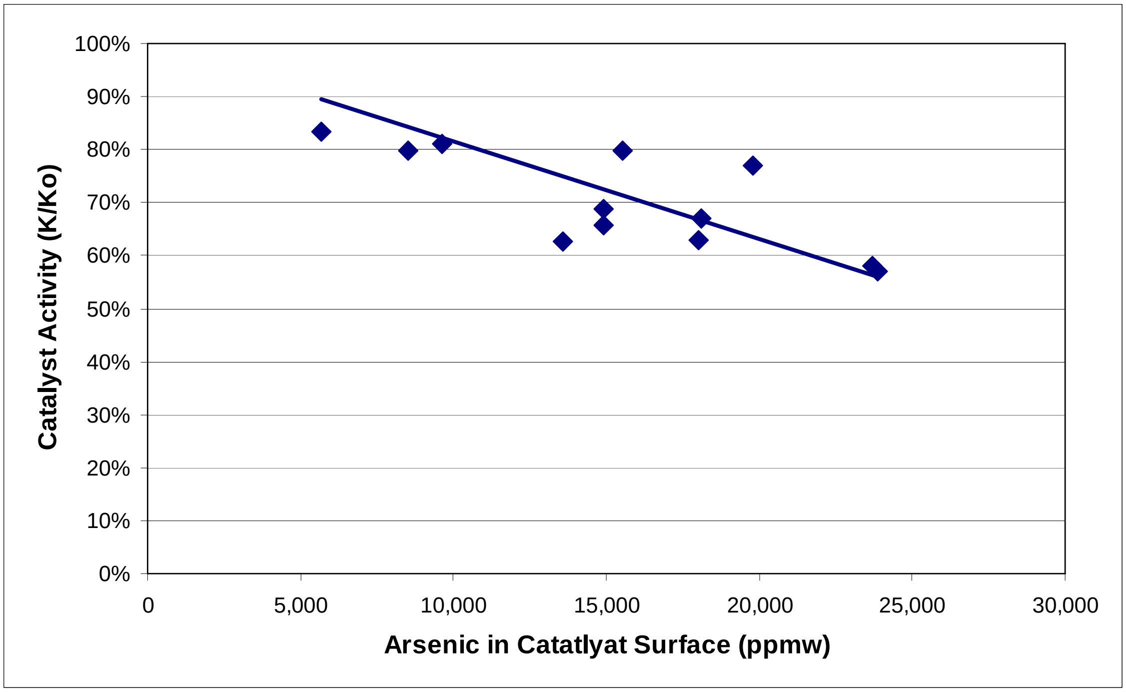

Figure 4-13
Surface Arsenic Concentration Effects on Catalyst Deactivation

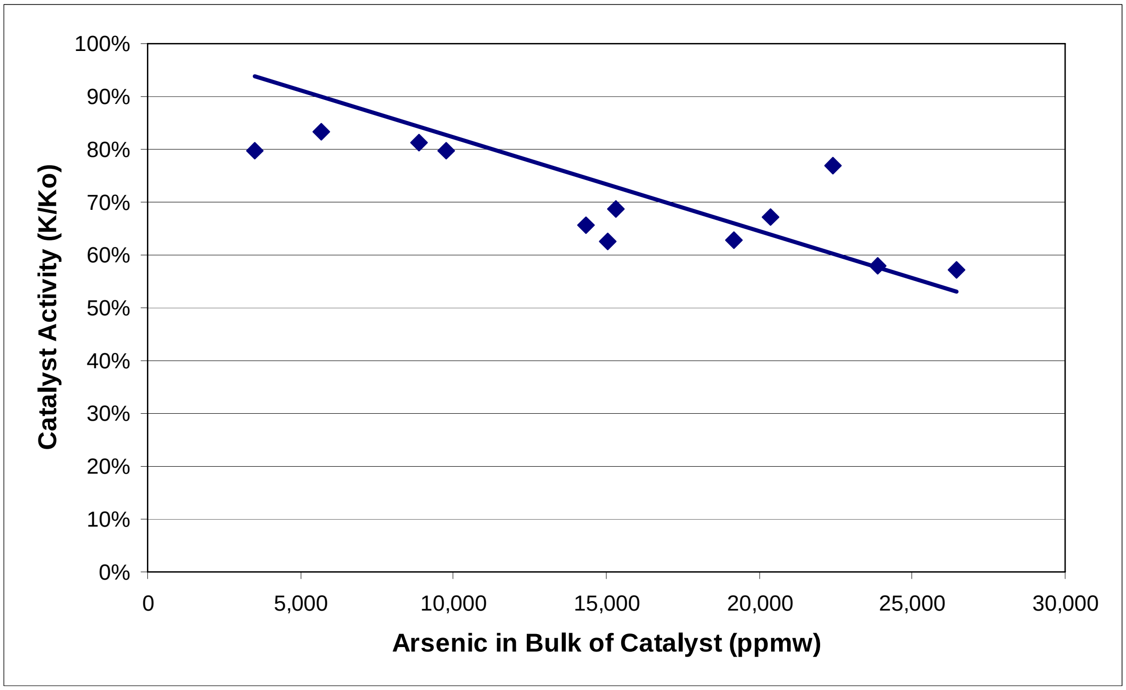

Figure 4-14
Bulk Arsenic Concentration Effects on Catalyst Deactivation

Figure 4-15 shows comparative surface and bulk arsenic concentrations for the twelve (12) samples used in the correlation. These data show that there is very little difference between the bulk and surface concentrations for most samples. This demonstrates the ability of arsenic to diffuse into the catalyst pore structure, attaching active vanadium sites throughout the bulk of the catalyst.

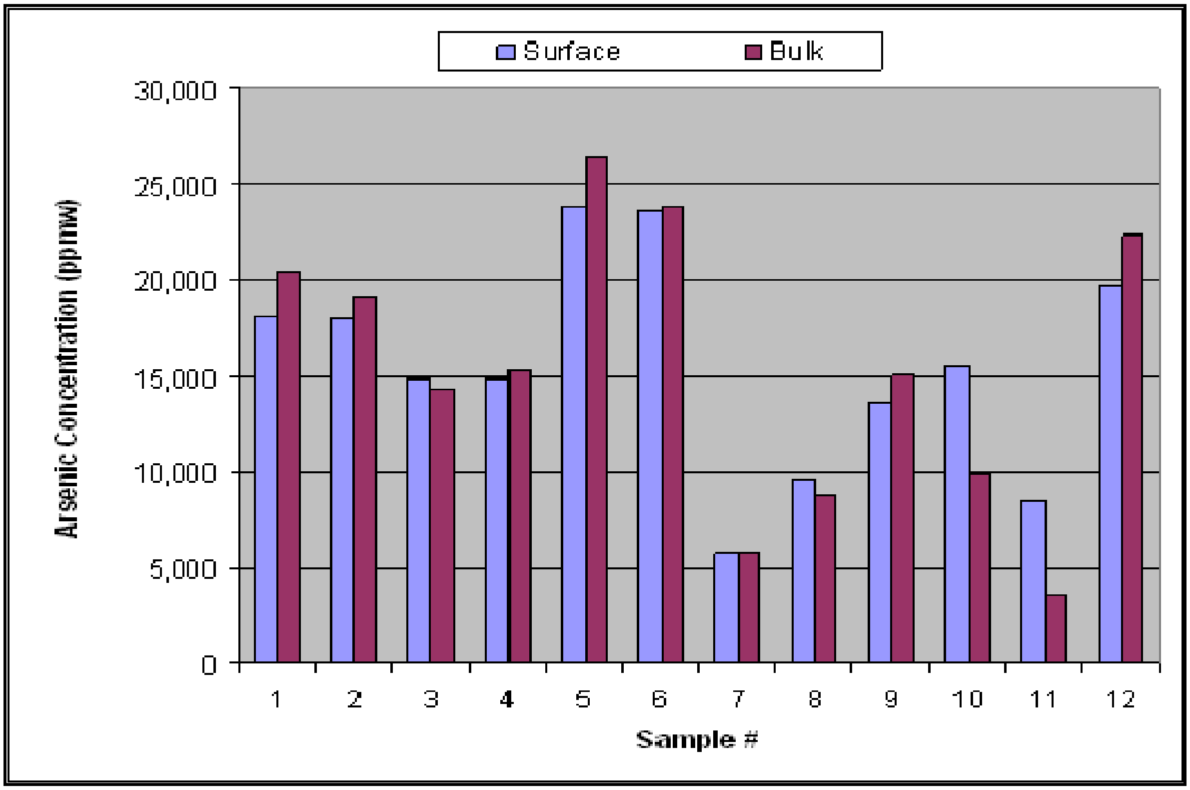

Figure 4-15
Comparative Surface and Bulk Arsenic Concentrations

5

CONCLUSIONS

This study evaluates the impacts of fuel type on plate type catalyst deactivation. As an approach, catalyst data (including activity, SO_2 conversion, and chemical composition) was obtained from EPRI members of the Post Combustion NOx Control Program, as well as data generated at Evonik's bench-scale test facility. The study has confirmed the primary modes of deactivation for common coal types currently being utilized in the Utility industry domestically; PRB, Southern Illinois bituminous, and Eastern bituminous.

Catalyst Deactivated on PRB Fuel

- The results showed that the most common mode of deactivation for most PRB coals will be calcium sulphate blinding/masking, which inhibits the ability of the reactants to reach the active catalytic sites on the catalyst surfaces. However, phosphorus poisoning heavily impacts deactivation and is in fact the controlling mechanism, as was the case with one of the presented case studies.
- Data indicated that the initial period of flue gas exposure, up to several thousand hours, produced an accelerated rate of catalyst deactivation, dropping to a relative activity of 50%. After the initial exposure period, the deactivation rate decreased possibly due to phosphorous saturation.
- Chemical analysis showed that phosphorous levels on the first and second layers were comparable. Similarly, both layers deactivated at the same rate. No information was available for the third or four layers.
- Data is subject to boiler operating impacts on phosphorous aerosol formation, and will apply to a single specific unit. More data will be needed to ascertain the impacts of phosphorous on catalyst deactivation.

Catalyst Deactivated on Bituminous Fuel

- With bituminous coals, the primary mode of deactivation will be arsenic poisoning, which is a chemical mechanism by which the active sites themselves are attacked by arsenic and rendered incapable of promoting the deNOx reaction. The data also showed that phosphorus poisoning was a factor with Southern Illinois bituminous fuel.
- Optimal fuels, such as eastern-bituminous coals which contain significant amounts of calcium, may result in catalyst lives which far exceed more onerous fuels, such as very high calcium PRB coal, or high-arsenic eastern bituminous coal. Thus the experienced catalyst life may vary dramatically from installation to installation. This can heavily affect the overall SCR system economics, as well as the general operability of the system (considering catalyst replacement outages, etc.).

- Arsenic concentrations in the catalyst were correlated to deactivation rates. The analysis included a total of 12 catalyst samples; all removed from the top layer and from different SCR reactors. Based on this data, it was estimated that activity will reach 60% when catalyst arsenic concentrations approximate 22,000 ppmw. It should be cautioned, however, that there are many modes of deactivation, and deactivation mechanisms other than arsenic could also impact catalyst life, including: ammonium bisulfate (ABS), erosion/attrition, thermal sintering, and ash fouling.

The study has highlighted the importance of catalyst testing. DeNOx activity and SO_2 conversion testing help to benchmark the catalyst's actual performance and rate of deactivation. Other testing, such as chemical composition testing, and other specialized testing, helps to confirm the modes of deactivation and assists in predicting the future deactivation rate for the particular application. Further, this testing helps in the early identification of operational and fuel-related problems, allowing them to be mitigated, where possible, to the greatest degree.

Overall, the project has helped to document actual catalyst deactivation mechanisms and rates experienced in the field on a variety of applications. The value of chemical analysis data in identifying the mechanism of deactivation was clearly demonstrated, and the data help to provide a basis for correlating fuel characteristic and catalyst chemical composition to the rate of deactivation. The information offers a benchmark to which various fuels and deactivation rates can be compared, and will assist utilities in determining the impacts that fuels will have on deactivation, helping to maximize catalyst life, and minimize adverse impacts.

A APPENDIX

Catalyst Test Results – Plate type catalyst deactivated on PRB fuels

SCR AND CATALYST INFORMATION	**R1**	**R2**	**R3**	**R4**
Catalyst Description				
Catalyst Type	Plate	Plate	Plate	Plate
Catalyst Pitch (mm)	6.52	6.52	6.52	6.52
Reactor Layer Position	1(top)	2 second	2 second	2 second
Vendor Designed Life	16000	16,000	16,000	16,000
New Catalyst Performance				
Activity (m/h)	46.3	46.3	46.3	46.3
SO_2 Conversion Rate (%)	0.4	0.3	0.3	0.3
Final Catalyst Performance				
Total hours in service (hrs)	7100	7100	7100	7100
Final Activity (m/h)	23.7	19.7	24.3	24.1
K/Ko	**51.19%**	**42.55%**	**52.48%**	**52.05%**
FUEL AND ASH ANALYSIS	**R**	**R**	**R**	**R**
Fuel Information (as-received)				
Fuel Type	PRB	PRB	PRB	PRB
Moisture	12	12	12	12
Co-fired fuels? / Frequency?	No	No	No	No
Ash Composition				
SiO_2	28.97	28.97	28.97	28.97
Al_2O_3	12.88	12.88	12.88	12.88
TiO_2	1.03	1.03	1.03	1.03
Fe_2O_3	4.6	4.6	4.6	4.6
CaO	26.5	26.5	26.5	26.5
MgO	5.09	5.09	5.09	5.09
K_2O	0.55	0.55	0.55	0.55
Na_2O	1.68	1.68	1.68	1.68
SO_3	12.3	12.3	12.3	12.3
P_2O_5	0.95	0.95	0.95	0.95
SrO	0.26	0.26	0.26	0.26
BaO	0.55	0.55	0.55	0.55
MnO_2	0.03	0.03	0.03	0.03
Fuel Arsenic to Ash CaO ratio	0.04	0.04	0.04	0.04
XRF CHEMICAL ANALYSIS RESULTS	F	F	F	F
Test Conditions				
Flue Gas Temperature (^{o}F)	693	693	693	693
Linear Velocity (act. m/s)	2.3	2.3	2.3	2.3
Area Velocity (m/h)	40.4	40.4	40.4	40.4
Inlet NO (ppmvd)	346	346	346	346
Inlet SO_2 (ppmvd)	206	206	206	206
O_2 (% dry)	3.2	3.2	3.2	3.2
H_2O (%)	12	12	12	12
Deactivated Chemical Composition	***Surface***	***Surface***	***Surface***	***Surface***
% SiO_2	7.5	8.2	**7.3**	7.8
% Al_2O_3	2.4	2.7	1.9	2.3
% Fe_2O_3	1.34	1.02	**0.63**	0.68
% TiO_2	49.2	39.8	67.4	59.6
% CaO	7	9.5	**3.2**	4.5
% MgO	1.23	1.07	1.01	1.66
% BaO				
% Na_2O	0.03	0.03	0.04	0.13
% K_2O	3.3	3.4	**0.67**	0.93
% SO_3	0.47	0.5	0.16	0.17
%P_2O_5	24.2	30.2	**11.1**	15.9
% V_2O_5	0.88	1.35	**2.7**	2.6
% WO_3	0.96	0.86	0.91	1.04
% MoO_3	0.88	1.13	2.8	2.4

SCR AND CATALYST INFORMATION	**R1**	**R2**	**R3**	**R4**
Catalyst Description				
Catalyst Type	Plate	Plate	Plate	Plate
Catalyst Pitch (mm)	6.52	6.52	6.52	6.52
Reactor Layer Position	2 second	2 second	2 second	2 second
Vendor Designed Life	16,000	16,000	16,000	16,000
New Catalyst Performance				
Activity (m/h)	46.3	46.3	46.3	46.3
SO_2 Conversion Rate (%)	0.3	0.3	0.3	0.3
Final Catalyst Performance				
Total hours in service (hrs)	50700	50700	50700	50700
Final Activity (m/h)	16.2	17.6	15.2	17.4
K/Ko	**34.99%**	**38.01%**	**32.83%**	**37.58%**
FUEL AND ASH ANALYSIS	**R**	**R**	**R**	**R**
Fuel Information (as-received)				
Fuel Type	PRB	PRB	PRB	PRB
Moisture	12	12	12	12
Co-fired fuels? / Frequency?	No	No	No	No
Ash Composition				
SiO_2	28.97	28.97	28.97	28.97
Al_2O_3	12.88	12.88	12.88	12.88
TiO_2	1.03	1.03	1.03	1.03
Fe_2O_3	4.6	4.6	4.6	4.6
CaO	26.5	26.5	26.5	26.5
MgO	5.09	5.09	5.09	5.09
K_2O	0.55	0.55	0.55	0.55
Na_2O	1.68	1.68	1.68	1.68
SO_3	12.3	12.3	12.3	12.3
P_2O_5	0.95	0.95	0.95	0.95
SrO	0.26	0.26	0.26	0.26
BaO	0.55	0.55	0.55	0.55
MnO_2	0.03	0.03	0.03	0.03
Fuel Arsenic to Ash CaO ratio	0.04	0.04	0.04	0.04
XRF CHEMICAL ANALYSIS RESULTS	F	F	F	F
Test Conditions				
Flue Gas Temperature (^oF)	720	720	720	720
Linear Velocity (act. m/s)	2.3	2.3	2.3	2.3
Area Velocity (m/h)	32.3	32.3	32.3	32.3
Inlet NO (ppmvd)	350	350	350	350
Inlet SO_2 (ppmvd)	150	150	150	150
O_2 (% dry)	4	4	4	4
H_2O (%)	11.5	11.5	11.5	11.5
Deactivated Chemical Composition	***Surface***	***Surface***	***Surface***	***Surface***
% SiO_2	8.1	7.2	7	7.3
% Al_2O_3	2.7	1.76	2.1	2.2
% Fe_2O_3	0.84	0.9	0.66	0.99
% TiO_2	36.1	68.7	67.6	62.2
% CaO	11.5	2.9	3.4	4.1
% MgO	1.76	0.86	1.13	1.59
% BaO				
% Na_2O	<.03	0.04	0.04	0.14
% K_2O	1.29	0.7	0.72	0.86
% SO_3	0.75	0.18	0.16	0.17
%P_2O_5	32.8	10.5	10.8	14.4
% V_2O_5	1.32	2.7	2.7	2.6
% WO_3	0.75	1.11	0.89	0.85
% MoO_3	1.39	2.4	2.69	2.4

B APPENDIX

Catalyst Test Results – Plate type catalyst deactivated on Illinois Basin Fuels

SCR AND CATALYST INFORMATION	**Q1**	**Q2**	**Q3**	**S2**	**S3**
Catalyst Description					
Catalyst Type	Plate	Plate	Plate	Plate	Plate
Catalyst Pitch (mm)	5.6	5.6	5.6	5.6	5.6
Reactor Layer Position	top	second	third	second	third
Vendor Designed Life	16,000	16,000	16,000	16,000	16,000
New Catalyst Performance					
Activity (m/h)	42	42	42	42	42
SO_2 Conversion Rate (%)	0.5	0.5	0.5	0.38	0.4
Final Catalyst Performance					
Total hours in service (hrs)	10,871	10,871	3,625	18,554	18,554
Final Activity (m/h)	28.8	31.6	33.4	22.5	32.5
Final SO_2 Conversion Rate (%)	0.5	0.4	0.4	0.32	0.22
K/Ko	**68.57%**	**75.24%**	**79.52%**	**53.57%**	**77.38%**
Fuel Information (as-received)					
Fuel Type	Bituminous	Bituminous	Bituminous	Bituminous	Bituminous
Moisture	11%	11%	11%	11%	11.00%
Arsenic (ppm) - Average	10	10	10	10	10
Co-fired fuels? / Frequency?	No	No	No	No	No
Ash Composition					
SiO_2	52.51	52.51	49.67	49.67	51.4
Al_2O_3	20.62	20.62	29.78	29.78	26.7
TiO_2	0.97	0.97	1.36	1.36	1.3
Fe_2O_3	14.41	14.41	11.23	11.23	12.5
CaO	1.8	2.97	1.84	1.84	1.5
MgO	0.96	0.96	1.21	1.21	1.22
K_2O	2.12	2.12	2.11	2.11	2.8
Na_2O	0.69	0.69	0.56	0.56	0.34
SO_3	2.85	2.85	0.95	0.95	1.5
P_2O_5	0.43	0.43	0.22	0.22	0.46
SrO	0.09	0.09			
BaO	0.07	0.07	0.18	0.18	
MnO_2	0.03	0.03	0.03	0.03	0.04
Fuel Arsenic to Ash CaO ratio	5.56	3.37	5.43	5.43	
XRF CHEMICAL ANALYSIS RESULTS	**Q1**	**Q2**	**Q3**	**S2**	**S3**
Test Conditions					
Test Method/Protocol	VGB	VGB	VGB	VGB	VGB
Flue Gas Temperature (^oF)	725	752	752	752	752
Linear Velocity (act. m/s)	8.52	8.52	8.52	8.52	8.52
Area Velocity (m/h)	29.85	29.85	29.85	29.85	29.85
Inlet NO (ppmvd)	250	250	250	250	250
Inlet SO_2 (ppmvd)	1050	1050	1050	1050	1050
O_2 (% dry)	3.5	3.5	3.5	3.5	3.5
H_2O (%)	11	11	11	11	11
Deactivated Chemical Composition	***Surface***	***Surface***	***Surface***	***Surface***	***Surface***
% SiO_2	8.9	14.2	11.3	18.1	17.8
% Al_2O_3	2.2	4.6	4.8	6.2	5.1
% Fe_2O_3	0.28	0.89	1.08	1.04	1.15
% TiO_2	79.5	66.3	71.2	56.6	60.1
% CaO	0.68	1.31	1.05	1.61	1.54
% MgO	0.51	0.43	0.37	0.59	0.42
% BaO					
% Na_2O	0.08	0.06	0.05	0.03	0.03
% K_2O	0.36	0.66	0.26	0.72	0.75
% SO_3	0.17	0.3	0.22	0.4	0.28
%P_2O_5	0.98	6.2	3.8	9.2	7.5
% V_2O_5	0.08	0.22	0.22	0.57	0.38
% WO_3	0.95	0.81	1.13	0.87	0.88
% MoO_3	4.10	2.6	3.2	2.4	2.9
As (ppm)	11,728	10800	9530	12700	9160

C APPENDIX

Catalyst Test Results – Plate Type Catalyst Deactivated on Eastern Bituminous Fuels

SCR AND CATALYST INFORMATION	**A1**	**A2**	**B1**	**B2**	**B4**	**D**
Catalyst Description						
Catalyst Type	Plate	Plate	Plate	Plate	Plate	Plate
Catalyst Pitch (mm)	6					
Reactor Layer Position	0 (top)	1 (top)	1 (top)	1 (top)	1 (top)	1
Vendor Designed Life	19,000	19,000	24,000	24,000	24,000	22,000
New Catalyst Performance						
Activity (m/h)	46.8	46.8	46.7	39.1	45.7	48.3
SO_2 Conversion Rate (%)	0.13	0.13	0.38	0.12	0.2	0.17
Final Catalyst Performance						
Total hours in service (hrs)	11,000	11,000	22,300	22,300	22,300	22,000
Final Activity (m/h)	31.4	29.4	30.7	26.9	26.1	28
Final SO_2 Conversion Rate (%)	0.23	0.28	0.67	0.58	0.69	0.16
K/Ko	**67.09%**	**62.82%**	**65.74%**	**68.80%**	**57.11%**	**57.97%**
Fuel Information (as-received)						
Fuel Type	Bituminous	Bituminous	Bituminous	Bituminous	Bituminous	Bituminous
Moisture	2%	2%	6%	6%	6%	6.30%
Arsenic (ppm) - Average	10	10	10	10	10	40
Co-fired fuels? / Frequency?	No	No	No	No	No	No
Ash Composition						
SiO_2	52.51	52.51	49.67	49.67	49.67	51.4
Al_2O_3	20.62	20.62	29.78	29.78	29.78	26.7
TiO_2	0.97	0.97	1.36	1.36	1.36	1.3
Fe_2O_3	14.41	14.41	11.23	11.23	11.23	12.5
CaO	2.97	2.97	1.84	1.84	1.84	1.5
MgO	0.96	0.96	1.21	1.21	1.21	1.22
K_2O	2.12	2.12	2.11	2.11	2.11	2.8
Na_2O	0.69	0.69	0.56	0.56	0.56	0.34
SO_3	2.85	2.85	0.95	0.95	0.95	1.5
P_2O_5	0.43	0.43	0.22	0.22	0.22	0.46
SrO	0.09	0.09				
BaO	0.07	0.07	0.18	0.18	0.18	
MnO_2	0.03	0.03	0.03	0.03	0.03	0.04
Fuel Arsenic to Ash CaO ratio	3.37	3.37	5.43	5.43	5.43	
XRF CHEMICAL ANALYSIS RESULTS	**A1**	**A2**	**B1**	**B2**	**B4**	**D**
Test Conditions						
Test Method/Protocol	BGV	BGV	BGV	BGV	BGV	BGV
Flue Gas Temperature (^oF)	711	711	705	705	705	703
Linear Velocity (act. m/s)	6.46	6.43				5.64
Area Velocity (m/h)	50.5	50.2	70	70	70	39.4
Inlet NO (ppmvd)	303	303	250	250	250	356
Inlet SO_2 (ppmvd)	3006	3007	400	400	400	627
O_2 (% dry)	3.3	3.3	5	5	5	4
H_2O (%)	8.4	8.5	10	10	10	9.5
Deactivated Chemical Composition	***Surface***	***Surface***	***Surface***	***Surface***	***Surface***	***Surface***
% SiO_2	22.8	17.79	19.3	19.8	23.6	10.4
% Al_2O_3	6.2	5.32	3.6	5.1	10.2	3.26
% Fe_2O_3	3.09	4.97	0.59	1.29	1.41	0.58
% TiO_2	50.8	56.4	66	61.6	50.3	76
% CaO	1.1	0.62	0.96	0.88	0.67	0.85
% MgO	0.42	0.24	0.45	0.49	0.63	0.42
% Na_2O	0.4	0.199	0.45	0.43	0.42	0.23
% K_2O	0.184	0.181	0.17	0.27	0.47	0.13
% SO_3	7.95	7.35	2.7	3.2	5.7	0.95
%P_2O_5	0.5	0.156	0.23	0.39	0.94	0.26
% V_2O_5	1.3	1.05	1	0.48	1.08	0.99
% WO_3	0.03	0.04	0.04	0.06	0.06	0.1
% MoO_3	2.5	2.77	2.7	3.7	1.67	2.5
As (ppm)	18,100	18,000	14,900	14,900	23,875	23,700

SCR AND CATALYST INFORMATION	**F1**	**F2**	**G1**	**G2**	**G3**	**G4**
Catalyst Type	Plate	Plate	Plate	Plate	Plate	Plate
Catalyst Pitch (mm)	5.7	5.7	5.7	5.7	5.7	5.7
Reactor Layer Position	1(top)	1(top)	1 (top)	1(top)	1(top)	1(top)
Vendor Designed Life	8,000	8,000	9,500	24,000	24,000	7,000
New Catalyst Performance						
Activity (m/h)	42.5	42.5	47	55.8	53.6	39.1
SO_2 Conversion Rate (%)	1.2	1	1.5	1.5	1.5	1.5
Final Catalyst Performance						
Total hours in service (hrs)	16,959	16,532	19,197	17,862	16,551	23,598
Final Activity (m/h)	35.4	34.5	29.4	44.5	56.3	30.1
Final SO_2 Conversion Rate (%)	0.4	0.4	0.73	0.91	0.9	0.37
K/Ko	**83.29%**	**81.18%**	62.55%	79.75%	79.75%	76.98%
Fuel Information (as-received)						
Fuel Type	Bituminous	Bituminous	Bituminous	Blend	Blend	Bituminous
Moisture	11%	11%	9.68	10.16	10.16	9.27
Arsenic (ppm) - Average	9.95	9.95	16.4	16.4	16.4	16.3
Co-fired fuels? / Frequency?	No	No	No	No	No	No
Ash Composition						
SiO_2	46.48	46.48	47.102	46.69	46.69	45.8
Al_2O_3	18.87	18.87	19.71875	21.9	21.9	20.9345
TiO_2	0.95	0.95	0.965	1	1	0.981
Fe_2O_3	21.562	21.562	22.88	21.69	21.69	21.224
CaO	4.294	4.294	2.472	2.76	2.76	3.319
MgO	0.908	0.908	0.83125	0.82	0.82	0.9246
K_2O	2.557	2.557	2.187	2.03	2.03	2.411
Na_2O	0.4985	0.4985	0.5155	0.53	0.53	0.4521
SO_3	3.706	3.706	2.64125	2.52	2.52	3.034
P_2O_5	0.19	0.19	0.18375	0.33	0.33	0.3123
SrO	0.0309	0.0309	0.0375	0.09	0.09	0.0607
BaO	0.064	0.064	0.06375	0.07	0.07	0.104
MnO_2	0.0416	0.0416	0.03875	0.04	0.04	0.0375
Fuel Arsenic to Ash CaO ratio	2.32	2.32	6.63	5.94	5.94	4.91
XRF CHEMICAL ANALYSIS RESULTS	**C**	**F**	**I**	**L**	**N**	**P**
Test Conditions						
Test Method/Protocol	VGB	VGB	VGB	VGB	VGB	VGB
Flue Gas Temperature (°F)	651	660	720	725	725	671
Linear Velocity (act. m/s)	5.71	5.83	5.3	5.4	5.4	5.36
Area Velocity (m/h)	31.9	32.4	28.2	28.8	28.7	29.6
Inlet NO (ppmvd)	250	240	322	230	230	220
Inlet SO_2 (ppmvd)	2000	2780	3376	2642	2642	2900
O_2 (% dry)	3.5	3.7	3.5	3.5	3.5	2.9
H_2O (%)	8	8.6	9.4	6.8	6.8	7
Deactivated Chemical Composition	***Surface***	***Surface***	***Surface***	***Surface***	***Surface***	***Surface***
% SiO_2	19	20.96	20	7.6	3.48	18.78
% Al_2O_3	4.23	5.17	8.59	6.1	2.85	8.24
% Fe_2O_3	1.46	1.56	1.79	1.6	1.43	2.86
% TiO_2	55.2	54	51.1	74.1	82.4	47
% CaO	2.42	2.4	1.55	0.22	<.1	2.25
% MgO	0.16	0.3	0.57	0.38	0.16	0.64
% Na_2O	0.38	0.49	0.57	0.19	<.1	0.5
% K_2O	0.56	0.25	0.31	0.15	<.1	0.36
% SO_3	11.57	9.1	9.44	1.8	2.09	12.49
%P_2O_5	0.23	0.36	0.66	0.17	0.115	0.87
% V_2O_5	1.16	1.19	1.11	1.6	1.64	1.07
% WO_3	<.1	<.1	<.1	<.1	<.1	<.1
% MoO_3	2.39	2.37	2.33	3.6	4.24	1.97
As (ppm)	5,692	9,616	13,600	15,513	8,513	19,797

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