THE GOALS, CHALLENGES AND SUCCESSES OF REGENERATING SELECTIVE CATALYTIC REDUCTION CATALYST

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ABSTRACT:

SCR-Tech was formed in the United States during 2001 by a consortium of European companies with significant experience in the management, testing and forecasting of SCR catalyst, which had developed and commercialized in Germany innovative and proprietary processes for the cleaning, regeneration and rejuvenation of SCR catalyst. These processes have been successfully applied in Germany since 1997 and since 2003 in the United States. In total, more than 14,000 m^3 of SCR catalyst has been regenerated / rejuvenated to date, validating the technology's ability to achieve maximum NOx reduction performance while reducing overall NOx compliance costs for the power generating facility.

Regenerations, which involve the complete cleaning and re-activation of the SCR catalyst, have been performed on all current catalyst types, including plate, honeycomb and corrugated catalyst. Both in Europe and in the U.S., entire fleets of SCR systems owned by utilities and independent power producers ("IPPs") utilize the proprietary regeneration process offered by SCR-Tech. In Germany, in particular, catalyst regeneration has captured approximately 70% of the catalyst replacement market. There, the three largest municipal utilities, the second, third and fourth largest investor-owned utilities, and the largest IPP all use catalyst regeneration throughout their entire fleets to minimize operating and maintenance costs. SCR-Tech's regeneration processes have also been applied to plants in Austria and Belgium. The regeneration process offered by SCR-Tech in the U.S. is marketed in Europe by ENVICA Kat.

In the United States, SCR-Tech offers catalyst regeneration, rejuvenation and cleaning services, as well as SCR catalyst management and consulting services to help power plant operators optimize their SCR system operation, improve NOx reduction performance, and reduce overall NOx compliance costs. These services include catalyst inspection and specification, performance and guarantee testing, general decay and SO_2 oxidation testing, surface and bulk chemical testing; and most importantly, catalyst life cycle forecasting through advanced computer simulation to provide guidance on effective catalyst management strategies. SCR-Tech also endeavors to further expand its spectrum of cost-effective environmental compliance solutions for SCR operators consistent with the ever changing

requirements for SCR catalyst. In keeping with this objective, SCR-Tech has initiated a program to optimize the parameters used in its regeneration process to achieve maximum restoration of catalytic activity while minimizing the conversion of SO_2 to SO_3. Preliminary results of a recently completed study, jointly conducted with AEP and Southern Company, demonstrated that the use of regenerated catalyst can lower SO_2 oxidation rates by as much as 40-50%. SCR-Tech is also beginning to examine the impact of its regeneration process on mercury oxidation rates. This paper reviews the past, examines the present and looks forward into the future of SCR catalyst management.

INTRODUCTION:

SCR-Tech was founded in the United States in 2001 by three German firms: ENVICA, one of the original developers of the catalyst cleaning and regeneration process; EnBW, one of Germany's largest utilities and a subsidiary of EDF; and E&EC, a German consulting company and sales and marketing partner. SCR-Tech initiated commercial operations in its state of the art regeneration facility in early 2003, and was subsequently acquired by Catalytica Energy Systems, Inc. in February 2004.

Today, SCR-Tech offers its customers broad power plant expertise through more than 100 years of combined experience in the environmental and power generation industries. SCR-Tech formed a new management team in 2005 that brings broad-ranging knowledge of the operation of coal-fired power plants, including all upstream and downstream equipment used with boilers, how each piece of equipment interacts, and the impact of the operation of one piece of equipment on another. By offering a complete understanding of boiler and environmental technology, along with its expertise in the operation of selective catalytic reduction systems and SCR catalyst, SCR-Tech is able to provide its customers a thorough and optimum approach to effective SCR and catalyst management.

SCR-Tech's headquarters along with its regeneration, warehouse and laboratory facilities are located in Charlotte, North Carolina. (See Figure 1).

CATALYST REHABILITATION:

SCR-Tech offers proprietary and patented processes based on highly sophisticated and advanced technologies that can improve the NOx removal efficiency and extend the useful life of installed SCR catalyst, offering a compelling economic alternative to catalyst replacement.

SCR-Tech's processes are capable of not only physically cleaning and rejuvenating the most severely plugged, blinded or poisoned catalyst, but of also chemically reactivating deactivated catalyst. Depending upon the state of the installed catalyst, SCR-Tech offers several alternatives for restoring its NOx removal efficiency and extending its life.

For lightly plugged or masked catalyst that has not yet fully deactivated from catalyst poisons, SCR-Tech offers an "in-situ" cleaning process that can be performed on catalyst at the customer's plant site without requiring removal of the catalyst from the SCR unit. This process is not recommended for large particle ash ("LPA") plugging.

For severely plugged or blinded catalyst that may have limited deactivation from catalyst poisons, SCR-Tech offers an off-site cleaning and rejuvenation process that is performed at SCR-Tech's facility. In this process, the customer removes the catalyst modules from the SCR unit and they are shipped to SCR-Tech. SCR-Tech's cleaning process physically removes the materials plugging the catalyst to improve its NOx removal efficiency while the rejuvenation process removes catalyst poisons to restore its remaining useful life. Once cleaned and rejuvenated, SCR-Tech returns the catalyst modules to the customer for reinstallation into the SCR unit.

For catalyst that has significantly deactivated and that may also be severely plugged or blinded, SCR-Tech offers an off-site regeneration process that restores deactivated SCR catalyst back to its original specifications and catalytic activity; often to activity levels beyond original (see Figure 2). Initially the catalyst is supplied with essentially two major activity components: 1) the necessary or basic activity to achieve the required NOx reduction performance at initial operation, and 2) additional or useful activity to allow the specification duty to be met through some useful life. These are depicted in the Ko (original activity) bar of Figure 2 as the gray and red regions, respectively. Aging of the catalyst reduces the useful activity through channel plugging and pluggage by ash, and by the blinding of the active sites on a microscopic scale by fuel constituents and other fuel-related poisons that attach to active sites, chemically deactivating or sealing them and rendering these sites impotent. These deteriorating factors reduce the catalyst activity until the useful life has been depleted. At that time, the catalyst must be replenished, either through the purchase of new replacement catalyst or through regeneration. Replacement is a more costly alternative and results in disposing of the basic activity still left in the catalyst. Regeneration, on the other hand, fully restores the useful activity of the spent catalyst, while still taking full advantage of all the basic activity, for approximately 60% the cost of replacement.

SCR-Tech's regeneration process involves removing the deactivated catalyst modules from the SCR unit and shipping them to SCR-Tech's regeneration facility where the catalyst is both cleaned and chemically reactivated (see Figure 3). Once regenerated (see Figure 4), SCR-Tech returns the catalyst modules to the customer for reinstallation in the SCR unit. Upon reinstallation, the regenerated catalyst delivers the same level of performance and deactivation rate as the original catalyst. Catalyst regeneration not only provides SCR operators a significantly lower cost alternative to catalyst replacement, it also eliminates the costs and environmental liabilities associated with disposing of deactivated catalyst, which must be shipped to a disposal site and may be considered hazardous waste. If some catalyst is too damaged to be reused and must be disposed of, SCR-Tech can ultrasonically clean the catalyst to remove all poisons prior to disposal to avoid the potentially high costs associated with hazardous waste. More information about the business case for SCR catalyst regeneration is contained in a recent article published in Power Magazine.[1]

CATALYST MANAGEMENT:

SCR-Tech also provides a wide variety of customized SCR catalyst management services to help power plant operators improve their SCR system performance and achieve cost-effective NOx compliance. These services include catalyst specification, selection and initial performance testing for guarantee verification, along with catalyst inspection, testing, computer simulation, and analysis plus verifying/remedying flow distribution and ammonia injection distribution. SCR-Tech also maintains a stock of regenerated catalyst to provide emergency or spare layers of catalyst to its customers.

SCR-Tech develops catalyst management plans for its customers consistent with catalyst activity decay, ammonia slip and scheduled outages, with the understanding that some plants market their ash. SCR-Tech's comprehensive catalyst management programs include performing inspections, ammonia injection grid tuning, computer simulation and tracking of catalyst decay rates, evaluating the effects of fuels fired, providing catalyst test programs and guidance on catalyst interchangeability between units with options for new, brokered, rejuvenated and regenerated catalyst for either a single unit, a plant site, or the entire fleet. As part of its catalyst management program, SCR-Tech offers a customized catalyst regeneration plan scheduled around planned outages

Catalyst management is often viewed as developing a plan for a given SCR system to maintain sufficient catalyst activity to achieve the required NOx reduction with an acceptable margin to avoid inadvertent NOx or ammonia slip excursions beyond allowable limits. Catalyst suppliers create "saw-tooth" charts to graphically depict the decline in NOx reduction performance of each catalyst layer over time and to manage their catalyst layers. However, these charts do not account for poor or deteriorating ammonia flow distribution, or for poor gas distribution. Although these factors can negatively impact the useful life of the catalyst, no factor in our experience is as detrimental as inefficient SCR operation or catalyst pluggage. In our experience, many SCR reactors have entrance configurations that allow the flue gas to overshoot the first few layers of catalyst, causing reverse flow and eddies at and above the catalyst closest to the boiler. Over time the ash accumulates, causing full pluggage of the catalyst channels and resulting in the formation of an ash pile (see Figure 5). As the catalyst modules closest to the boiler plug, the overshoot of flue gas moves further from the boiler and slowly the pluggage works its way toward the catalyst modules at the rear of the reactor. As the catalyst channels become plugged, flue gas can no longer flow through. As a result, the velocity of the flue gas through any remaining open channels degrades the catalyst activity at a higher rate and increases the erosion potential within the catalyst modules. Pluggage on the top layer will eventually impact the catalyst layer below, which will begin to experience the same problem. As catalyst modules get more and more plugged, the reactor must eventually be taken off line. This phenomenon has been tracked by measuring the pressure drop across individual catalyst layers. Experience has shown some top layers had the pressure drop increase more than three fold due to pluggage. The only long term solution to poor flow distribution is reevaluating the flow design and revising it. This is not a simple or quick task, and a large scale flow model may be advisable.

Another problem is the accumulation on the top layer of LPA (see Figure 6), also referred to as popcorn ash. The formulation and accumulation of this ash is believed to be the result of either poor combustion and/or high furnace exit gas temperature compared to the ash fusion temperature. Normally, these conditions might occur from switching to low NOx burners or switching fuels. LPA can settle on the top layer of catalyst or wedge within the channels. Again this pluggage can cause considerable SCR operational problems. There has been some success by others in using ash screens to prevent the LPA from reaching the SCR[2]. Burner retuning, the use of screens along with proper flue configuration and gas velocities appear to be the best solution to mitigate this problem.

The fuels fired can also have a major impact upon the SCR catalyst performance. Thus, before switching fuels, the catalyst and the fuel require a thorough review. Arsenic, for example, is a major problem that can be caused by firing eastern bituminous coal. Arsenic forms vanadium arsenate, which can result in the loss of the active vanadium sites as the NOx, ammonia and oxygen cannot use a site that is tied up by arsenic. The impact of arsenic on the rate of SCR catalyst deterioration highly depends upon two factors. The first is the quantity of arsenic in the coal. Higher arsenic concentration increases the catalyst degradation rate. The second factor is the amount of free calcium in the ash, which can mitigate Arsenic. Thus, if sufficient calcium is present, the impact of the arsenic may be overcome. Some high arsenic coals are fired with limestone mixed in to add sufficient calcium and avoid excessive catalyst poisoning. More detailed presentations of arsenic poisoning are available[3]. Although calcium is desirable when firing eastern bituminous coal, it can be the major source of catalyst deterioration for Powder River Basin ("PRB") coals. Here the CaO enters the catalyst porosity and, with SO_3, form $CaSO_4$. This sulfate is larger than the CaO and clogs the catalyst channels, preventing the NOx, ammonia and oxygen from entering. As a result, the active sites within the catalyst channel are lost.

Some SCR systems suffer from poor ammonia distribution. This often occurs with larger ammonia injection grids ("AIG") containing a large number of nozzles. Once the SCR is put into service, the AIG is "tuned", that is, the flow to the nozzles is adjusted to get an even distribution of ammonia with respect to the NOx in the flue gas stream. This is usually accomplished by measuring the NOx at an outlet grid and adjusting the ammonia flow from the AIG to obtain a uniform NOx outlet distribution. The downside of this approach is that over time, various factors such as the firing of different burners and coals in the furnace, changing loads or burner setting drift, could result in a change in the NOx distribution within the flue gas. When this occurs, the AIG must be retuned. To mitigate these shortcomings, more suppliers are moving toward an AIG with fewer nozzles but adding gas mixing after the AIG. In this scenario, a reasonably homogeneous mixture of gas, NOx and ammonia is sent to the SCR under all operating conditions and changing factors. Many plants have economizer bypass systems to keep the flue gas temperature above the ammonium bisulfate formation temperature at low load operation. In this case, the mixers should be positioned downstream of the introduction of hot bypass flue gas to assist in creating a uniform temperature for the SCR.

Maintaining the SCR effectiveness between outages also is a major factor in catalyst management. Mixing and matching catalyst across units or an entire fleet to minimize overall catalyst usage is also an important aspect of maintaining SCR effectiveness. Once the problems noted previously have been resolved or no longer present a significant factor in effective operation of the SCR system, the "saw-tooth" catalyst management chart can be very useful. Figure 7 is such a chart depicting a four layer reactor where three layers always have catalyst, and is representative of customers serviced by SCR-Tech. In this example, the first layer to be removed was layer 1, the top layer. A regenerated layer was added to the empty layer 4. Of note, the regenerated layer added to the empty layer 4 was from another reactor and was comprised of honeycomb catalyst, while the original three layers were plate type catalyst. The SCR would subsequently be placed back on line with the lower three layers having catalyst and the top layer empty. While the SCR was back in operation, the removed layer 1 was regenerated and subsequently installed back into its original position during another scheduled outage. At that time, layer 2 was due for catalyst replenishment. Layer 2 was removed at the same time that layer 1 was reinstalled; leaving layers 1, 3 and 4. The reactor returned to service while layer 2 was regenerated. The dotted lines reflect anticipated results based upon the results to date. This approach has been very successful for this particular plant because a sufficient number of catalyst performance tests were conducted early in the SCR life to allow for accurate predictions of catalyst degradation. These tests are depicted in the chart as small circles. Another factor contributing to the operational success of the SCR at this particular plant is that the unit has consistently been operated with the same fuel and in the same manner. Thus, past experience is directly applicable to present and future operation. Should any factors affecting SCR performance change in the future, a reevaluation of the catalyst management plan and additional catalyst testing would be in order.

For entire fleets of SCRs that fire different fuels, catalyst management can take on new meaning. Catalyst that has retained considerable activity but whose performance has been compromised by the firing of heavy oil, pet coke or orimulsion (rendering its surface high in vanadium sulfate, thereby raising its SO_2 oxidation to unacceptable levels), can be used elsewhere. Placing this catalyst in an SCR system fired by low sulfur fuels, such as PRB coal, can extend its useful life without any additional catalyst cost. It is through thorough knowledge of the fleet that maximum savings can be achieved.

SUCCESSES:

SCR-Tech's catalyst regeneration process is proven. Over the past nine years, more than 14,000 m^3 of SCR catalyst have been regenerated worldwide, including plate, honeycomb and corrugated configurations and spanning all major manufacturers: Hitachi, CERAM, Cormetech, BASF, Kawasaki, Argillon/Siemens, KWH and Haldor Topsoe. This regeneration experience encompasses in excess of 20,000 MW of power generating capacity and more than 8,000,000 hours firing bituminous, lignite and oil/gas fuels. As previously mentioned, catalyst regeneration has captured 70% of the catalyst replacement market in Germany.

SCR-Tech has successfully regenerated in the U.S. all catalyst types, achieving maximum restoration of Ko while often decreasing the SO_2 to SO_3 oxidation. Most recently, as part of the joint study with AEP and Southern Company, an independent third party laboratory confirmed that a regenerated honeycomb catalyst demonstrated full restoration of the original Ko while achieving a 57% reduction in SO_2 to SO_3 conversion when compared with new catalyst. These results prove that high activity levels are achievable while simultaneously reducing the oxidation rate.

As part of its development partnership with AEP and Southern Company, SCR-Tech is gaining further understanding of the impact of its regeneration parameters on the oxidation of SO_2 to SO_3. For the study, five significant regeneration parameters were chosen. A sixth parameter, catalyst type, was also included as AEP was more interested in plate type catalyst while Southern Company was more interested in honeycomb catalyst. Assuming six independent variables connected linearly, a total of 64 independent regenerations normally would be required. The time to perform these regenerations combined with the cost and time to test each outcome for activity, SO_2 oxidation and chemistry was prohibitive. Thus an experimental program was conducted using a six-factor, two-level ¼ fractional factorial design at resolution 4. This approach would resolve all primary factors. Additional details about the design of the study and testing is contained in a recent article published in Power Engineering Magazine[4].

As part of the study, new, unused plate and honeycomb catalyst modules were regenerated to compare the oxidation rate and catalytic activity before and after regeneration. After regeneration, the plate catalyst demonstrated a 66% reduction in SO_2 to SO_3 oxidation with only a slight decrease in original activity. The regenerated honeycomb catalyst achieved a 14% increase in activity without any change in oxidation rate. These preliminary results successfully demonstrate that the balance between catalytic activity and oxidation rates can be improved very significantly, but that more investigation is required to achieve an optimal balance.

Figure 7 depicts a catalyst regeneration program for one of SCR-Tech's customers that has been very successful through three regenerations. For each regeneration performed, an improvement in activity has been obtained while keeping the rate of SO_2 to SO_3 oxidation within acceptable limits. This regeneration program has been in effect for approximately three years.

CHALLENGES:

With increasingly stringent environmental regulations scheduled to take effect within a relatively short period of time, it is expected that a majority of the coal-fired power plants operating in the U.S. will be required to begin operating their SCR reactors on a year-round basis. While year-round operation will serve to further reduce NOx emissions in line with impending air quality standards, the industry is now becoming increasingly concerned with the conversion of sulfur dioxide (SO_2) to sulfur trioxide (SO_3) as a byproduct of operating SCR systems, and its related corrosive costs. At the same time, new regulations targeting emissions of Mercury are also being imposed, creating an even bigger challenge for coal-fired power plant operators.

SCR-Tech plans to build on the results gathered in its recently completed study with AEP and Southern Company to achieve an optimal balance between catalytic activity and SO_2 to SO_3 oxidation. At the same time, SCR-Tech expects to expand this program to evaluate the impact of regenerated SCR catalyst on the oxy-chlorination of mercury. It is believed that regeneration will have a positive impact on the catalyst's ability to oxidize mercury, and SCR-Tech aims to validate this belief.

A significant number of SCR systems continue to experience large particle ash pluggage. SCR-Tech has the ability and is developing improved technique for removing the pluggage. Preliminary results with this technique have proved very successful.

As noted above, with the onset of new environmental regulations, it is expected that SCR operation will soon be required on a year-round basis. As a result, catalyst will either need to be replaced or regenerated on a much more frequent basis, and effective catalyst management programs will be required to achieve cost-effective SCR operation while maintaining compliance with increasingly stringent NOx requirements.

In addition to offering a more cost-effective regeneration alternative to catalyst replacement, SCR-Tech maintains a stock of more than 500 MWe of regenerated SCR catalyst to provide its customers with emergency or spare layers of catalyst on an immediate basis. As SCR-Tech's business expands, this inventory is expected to grow. SCR-Tech also offers storage of catalyst for clients.

GOALS AND CONCLUSIONS:

SCR-Tech offers a proven and economically compelling alternative to purchasing new catalyst, along with more than 100 years of power industry experience to assist its customers with effective catalyst management programs. In addition, SCR-Tech is committed to expanding its spectrum of cost-effective environmental compliance solutions for SCR operators. In this regard, SCR-Tech is working to maximize SCR catalyst activity while minimizing SO_2 to SO_3 oxidation, and plans to evaluate the impact of its regeneration process on mercury oxy-chlorination. Additionally, improved methods of cleaning and rejuvenating catalyst are in process, with a focus on enhancing its processes for the effective removal of LPA. Simultaneously, SCR-Tech is working to improve its production throughput to better serve its customers as business grows, all the while consistently maintaining its high quality standards.

Effective SCR operation and catalyst management can become overwhelming for power plant operators from both a financial and human resource standpoint. With increasingly stringent air quality regulations soon to take effect, these resources are expected to be taxed even further. Minimizing overall costs for a single SCR system or for large fleets requires an intimate knowledge of catalyst, its replacement, rejuvenation and regeneration cycles, and how a plant's upstream and downstream equipment and fuels fired can play a factor in its performance. Effective catalyst management often means cutting ties with a "one size fits all" approach. The best and / or most cost-effective solution often results from flexibility in catalyst selection, methods of replenishment, and an informed management approach.

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FIGURES:

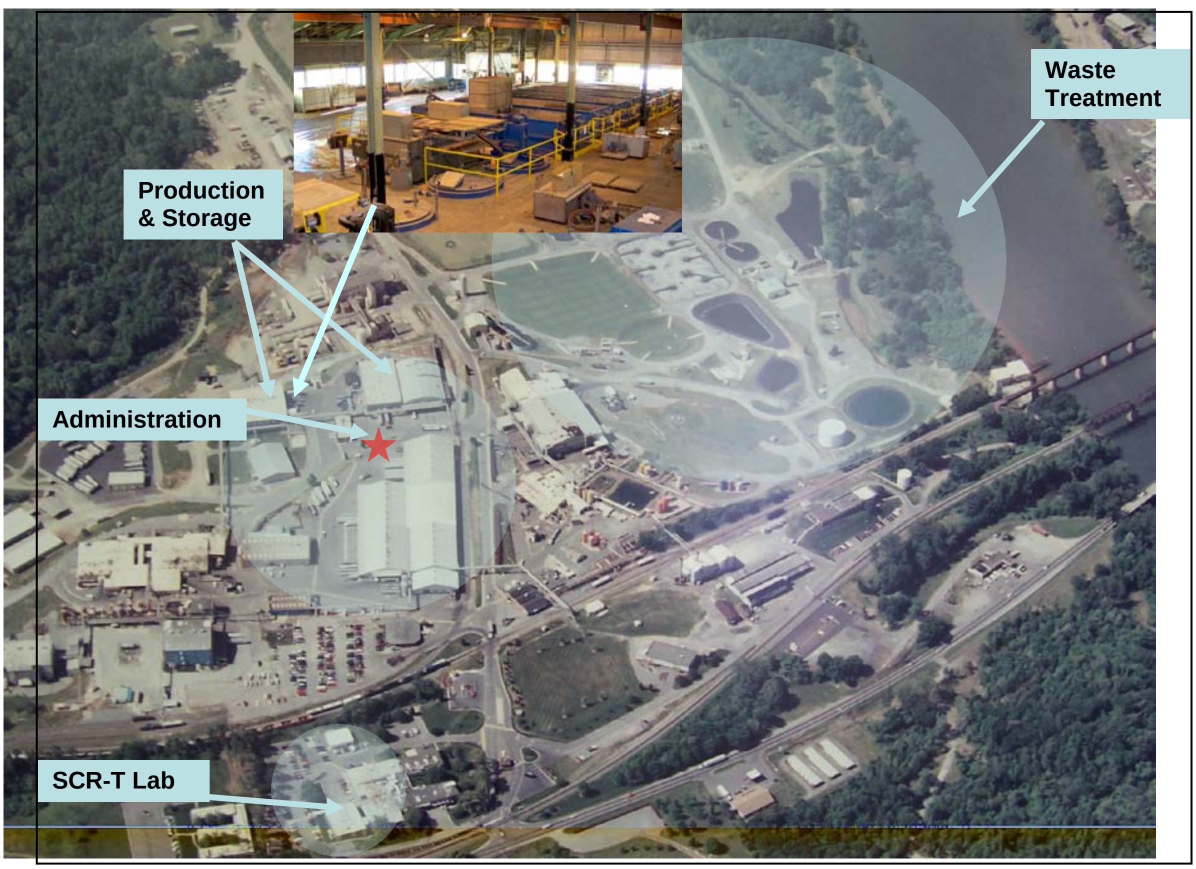

Figure 1: SCR-Tech Facility

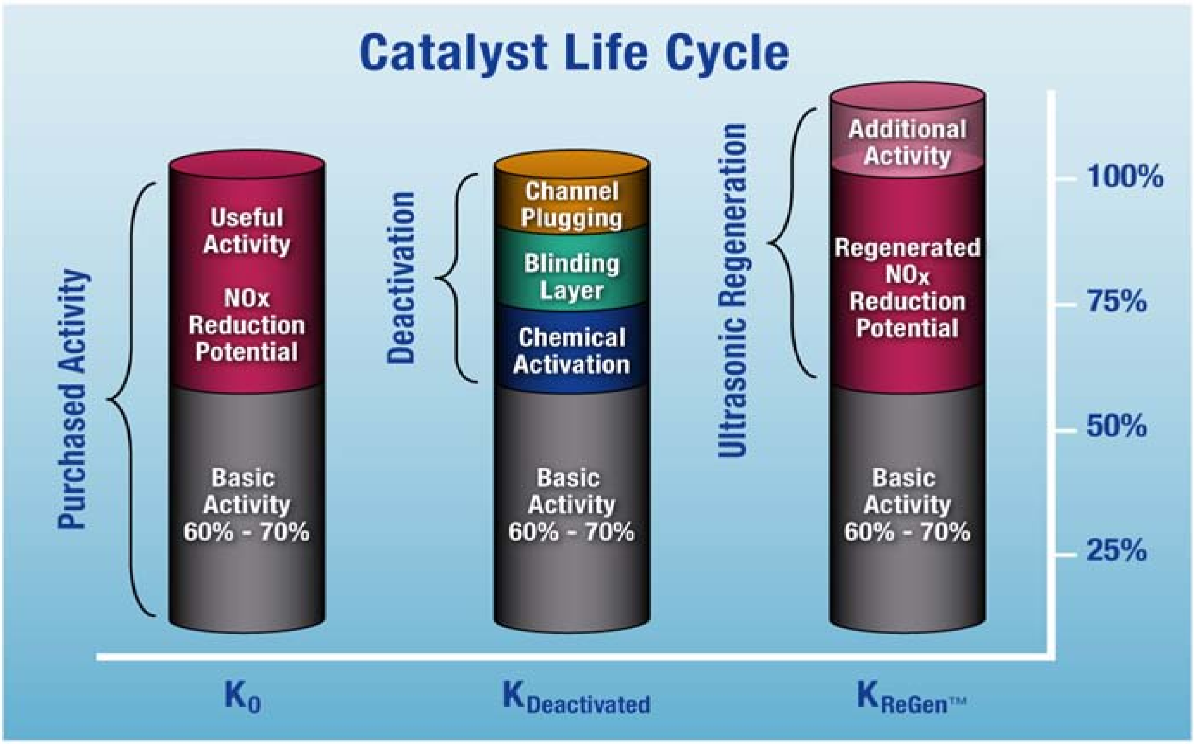

Figure 2: Catalyst Activity Distribution

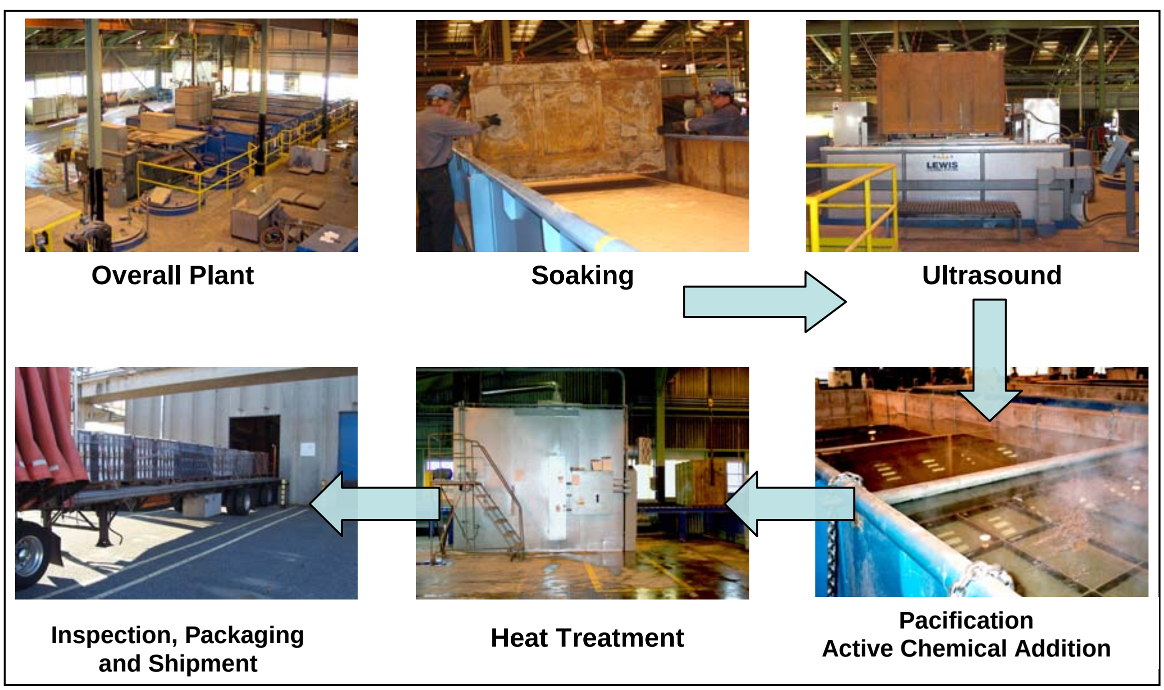

Figure 3: Patented Cleaning & Regeneration Process

Figure 4: Honeycomb, Plate and Corrugated – Before and After

Figure 5: Typical Ash Accumulation in SCR Catalyst Boiler Side

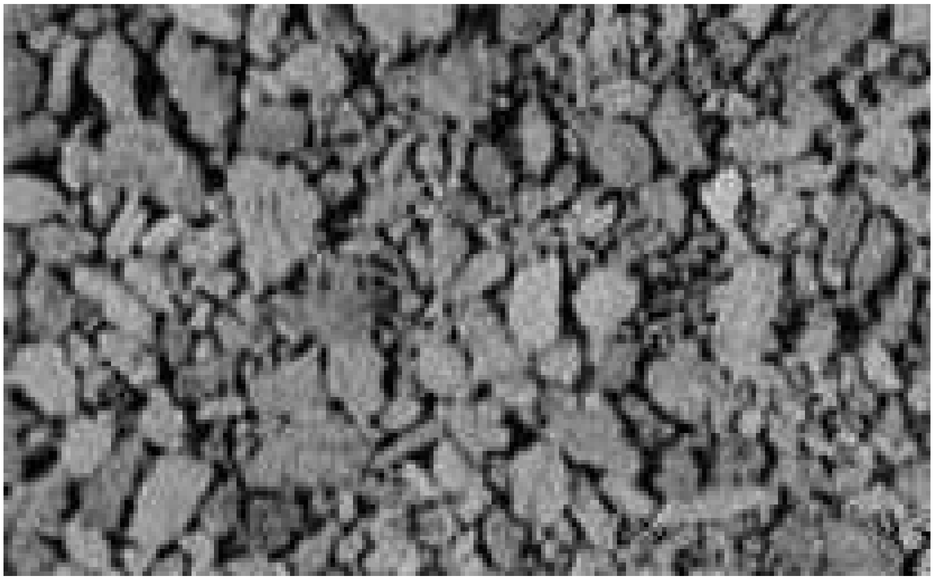

Figure 6: Typical Large Particle Ash

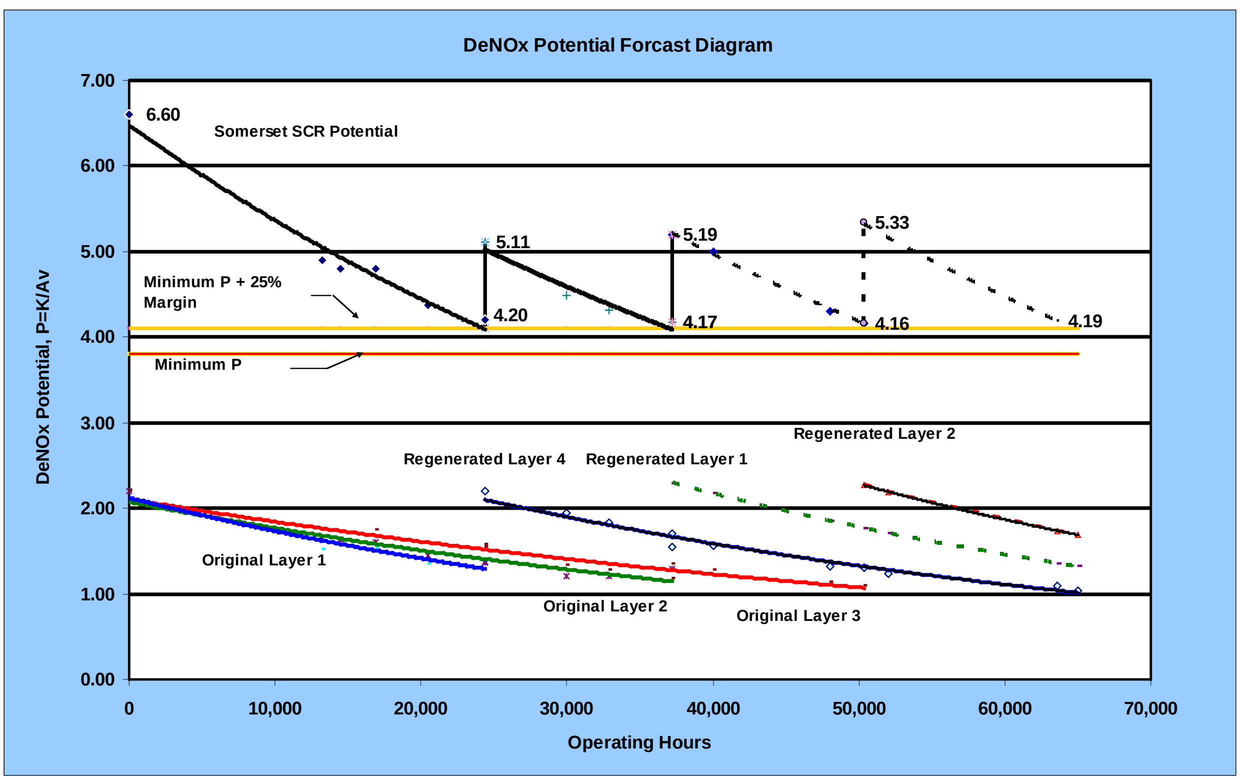

Figure 7: Typical “Saw-Tooth” Catalyst Management Curve