



SCR Catalyst Regeneration - 10 years of R&D Development and Commercial Application



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ABSTRACT

With year round SCR operation a widespread use of catalyst regeneration will minimize catalyst replacement costs. Evonik has more than ten (10) years of R&D and full scale catalyst regeneration experience. The paper explains developments over the last ten (10) years in catalyst regeneration to the current most advanced state-of-the-art regeneration process. Full scale regeneration results for all types of commercially available catalyst including:

- Full activity recovery for an application burning high sulfur Southern Illinois Basin coal.
- Opportunities to increase activity above the original value for an application burning world market compliance coal.
- SO₂/SO₃ conversion rate reduction for an application burning high sulfur Southern Illinois Basin coal.
- Mercury oxidation for an application burning mid-sulfur Southern Appalachian coal.
- Catalyst longevity (number of regeneration cycles) covering catalyst that was regenerated for the fourth time after about 100,000 SCR operating hours.
- Maintaining mechanical catalyst strength and structural integrity.

INTRODUCTION

Southern Company and Evonik Energy Services have a variety of programs underway to better understand the influencing factors and interactions of pollutants to the Selective Catalytic Reduction (SCR) and the SCR catalyst. This is primarily being driven by environmental legislation to reduce the emissions from coal fired units in the United States and around the world.

Early emissions legislation focused on sulfur dioxide (SO₂) and nitrous oxide (NO_x) reductions in the 1980's and 1990's. These pollutants were the primary contributors to acid rain and were the focal point of the EPA and legislature.

In the late 1990's and throughout 2000, the EPA focus has been on the acid mist, greenhouse gases and mercury emissions from coal fired power plants. The SCR is of particular interest as the catalyst will release oxygen and provide co-benefit to the oxidation of other pollutants which can be removed in an oxidized form where not easily removed in the elemental, such as mercury. Unfortunately, it can also oxidize pollutants, like sulfur dioxide to sulfur trioxide, which were in a form to be captured, however, converted to a form much more difficult to remove.

With the pending and established environmental regulations, the need for co-benefit applications within the SCR has become almost a necessity. As wet flue gas desulfurization (wFGD) systems come on-line and the units switch to a higher sulfur coal, the SCR is looked upon to provide co-benefit, particularly to help with mercury removal. It is well established that along with NO_x

reduction, SCR technology has potential for oxidizing mercury thereby providing enhanced removal in downstream wFGD systems.

Southern Company has conducted testing at its slip stream reactor located at one of its generating stations which is a 150 MW, T-Fired unit of the 1950's vintage. This unit is located at a generating plant in the southeastern portion of the United States. The coal that is fired is a high-Btu eastern bituminous coal, with a sulfur content of roughly 1.5%. Coal mercury levels were relatively consistent, ranging from approximately 150 to 200ppb.

The pilot equipment consisted of three identical parallel reactors. Each reactor was equipped with a dummy layer (flow straightening grid), and two layers of catalysts. The internal reactor dimensions were approximately 13" square. Catalyst "baskets" were constructed, each consisting of four (4) standard honeycomb elements, for a total of eight (8) elements per reactor (two baskets/layer x 4 elements each). The height of the catalyst was consistent with full-scale applications at slightly over 1 meter.

The facility was designed for a nominal reactor operating temperature of 700 °F, with temperature being controlled with in-line electric heaters. Depending on inlet gas temperature and flow rate requirements for a test condition, other temperatures may be obtained. Each reactor had a nominal design flow of 400 scfm (68 °F, 1 atm). To induce flow through the reactors, a tail-end fan and primary inlet dampers are installed to control the flow.

Evonik Industries, Energy Group currently operates over 10,000 MW's of coal fired capacity in four different countries and is faced with similar environmental issues. The SCR's in the fleet include seventeen (17) high-dust, six (6) low-dust and one (1) tailing end with operating experience of over 20 years on a 12 month x 24 hour operation per year.

Being an independent power producer, cost effective solutions are required to maintain a competitive posture. Through its engineering support group an extensive amount of analysis has been done to develop the low cost solutions.

This paper combines the understandings of both organizations in regards to operation of the SCR and its capabilities to assist and enhance the capture of the various pollutants.

BODY

In the Midwest, there has been a significant amount of activity in the installation of wet flue gas desulphurization (wFGD) systems for the capture of sulfur dioxide (SO₂). This is in an effort to meet the Clean Air Interstate Regulations (CAIR) which for geographic purposes is limited to states east of the Mississippi River. Prior to these installations (with the vast majority operational by 2010), the units were firing a higher cost, lower sulfur, environmental compliance or near compliance coal. With the wFGD systems, the units have the ability to utilize lower cost, higher sulfur fuels and still meet the environmental requirements.

In addition to the wFGD systems, SCRs were also installed as part of the Clean Air Act of 1990 and the CAIR requirements. With the conversion back to the higher sulfur fuels, the sulfur dioxide (SO₂) to sulfur trioxide (SO₃) conversion rate of the catalyst can become critical. The

SO₃, a particle size less than 2 microns (acid mist), is not captured in a wFGD system. With an emission rate of greater than 8 ppm, a visible “blue” plume from the stack is produced. Efficient operation of the SCR and more particular, the optimized SCR catalyst management becomes more critical.

Midwestern Fuel

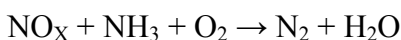
Many of the units that are installing wFGD systems will be converting from a lower sulfur compliance coal to a Midwestern higher sulfur fuel (Illinois or western Kentucky fuel). The Midwestern fuels tend to have much higher levels of arsenic and sulfur. Many of the units are firing a blend consisting of Western PRB fuels with lower sulfur Eastern fuels to meet the environmental mandates. The higher levels of arsenic in the eastern fuels are partially mitigated by the higher levels of calcium in the PRB fuels. This has the benefit of extending the life of the SCR catalyst.

In 2010, the emissions levels of CAIR affected plants will have to be further reduced which will require the installation of wFGD systems on the larger size units.

Fuel Influences

Catalyst performance and flue gas effects on the SCR catalyst are influenced by a variety of constituents in the fuel and their level of content within the fuel. The primary constituents that have a significant impact are: arsenic, calcium, iron, nitrogen, potassium, sulfur, and sodium.

The catalyst is comprised mainly of titanium oxide, molybdenum (plate type catalyst) or tungsten (honeycomb type catalyst), and vanadium pentoxide (V₂O₅). The vanadium pentoxide (V₂O₅) will release oxygen to the ammonia converting the nitrous oxide to nitrogen and water.



There are two different ways the effectiveness of oxygen release of the SCR catalyst can be minimized. The first is called catalyst poisoning; a substance attaches or combines with the vanadium pentoxide (V₂O₅) to form another compound which eliminates the potential for the release of the oxygen. The second is blinding or the plugging of the pores of the catalyst which prevents the ammonia from reacting with the vanadium pentoxide (V₂O₅). Poisoning or blinding both serve the same function of reducing the potential or “life” of the catalyst.

The common constituents in the fuel that cause poisoning are arsenic and phosphate. These constituents will combine with the vanadium to tie up the oxygen to prevent the oxygen release for the NO_x or other constituents.

The blinding constituents consist of calcium, sodium, and potassium and in essence plug the pores of the catalyst to prevent ammonia / nitrous oxide from coming into contact with the vanadium pentoxide (V₂O₅) catalyst material.

The sulfur in the fuel converts primarily to sulfur dioxide with a small amount to other species including sulfur trioxide (SO₃). Typically, the amount of SO₃ is approximately 0% - 0.2% of the total SO_x from the combustion process.

The SO_3 combining with water will form sulfuric acid, hence acid gas. With an SO_3 content above 10 to 20 ppm a “blue plumb” will be noticed from the stack. The blue plumb is dependent upon the stack diameter, and ambient air conditions.

As an example, a Midwestern medium sulfur fuel would be about 2000 ppm of SO_2 . This would equate to about 0 - 4 ppm of SO_3 emitted which would not cause a blue plumb.

SCR Design

The most common SCR designs that were deployed in the United States over the last ten (10) years are area a 3 or 4 layer design (see Figure 1). It was customary to install catalyst with one layer of the reactor spare. As there is a decay in the potential of the catalyst (ability to convert the nitrous oxide), the additional layer is installed. With this additional layer, the SO_3 will likewise increase.

Referring to the ‘blue plume’ SO_3 example without an SCR, the SO_3 was approx. 4 ppm. With the addition of a 2 x 1 SCR arrangement with a 0.5% conversion rate catalyst, each layer will contribute an additional 10 ppm of SO_3 . The two layer arrangement will increase the SO_3 from 4 ppm to roughly 24 ppm. Thus, adding another layer of catalyst would require additional reagent to mitigate the “blue plume” stack effect which in turn would require some type of SO_3 mitigation system to eliminate the visible plume.

What we have seen is that customers are looking at a strategy to minimize the layers installed in the SCR to minimize the SO_3 emissions or the size of the SO_3 mitigation system. In addition, they are looking for ways to reduce the SO_2 to SO_3 conversion rate of the catalyst or purchasing lower conversion rate catalyst.

NO_x / SO_3 Catalyst Reaction

Understanding how the various reactions occur provides thoughts and concepts for minimizing the SO_3 conversion rate.

The catalyst is produced by the original catalyst manufacturer (OCM) by mixing a somewhat homogeneous compound of ceramic, the titanium dioxide, vanadium and either molybdenum and/or tungsten. The ceramic material is either pressed onto a substrate layer of stainless steel mesh (plate type catalyst), extruded (honeycomb type catalyst) or manufactured similar to cardboard (corrugated type catalyst).

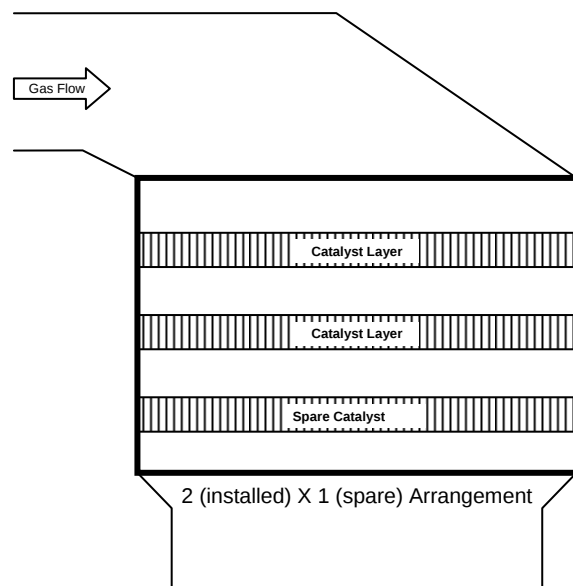


Figure 1: SCR Arrangement

The catalyst surface is constructed with a series of pores to provide a greater surface area. This minimizes the total volume of the catalyst required in the reactor to meet the removal requirements.

The SO_2 to SO_3 conversion rate is dependent upon a number of variables including available surface area in the catalyst pores, reactor temperature, and catalyst wall thickness. The NO_x reaction has precedence over the SO_2 to SO_3 conversion and will react with the oxygen released from the vanadium pentoxide (V_2O_5) more readily.

Both the SO_2 to SO_3 conversion as well as the NO_x reaction occur at greater temperatures. However, these two reactions are directly opposite one another for the SCR requirements.

In Figure 2, the NO_x / Ammonia (NH_3) / vanadium pentoxide (V_2O_5) reaction occurs near the outer surface within ~0.150 to 0.200 mm; below 0.200 mm, the SO_3 reaction occurs due to the slower reaction time.

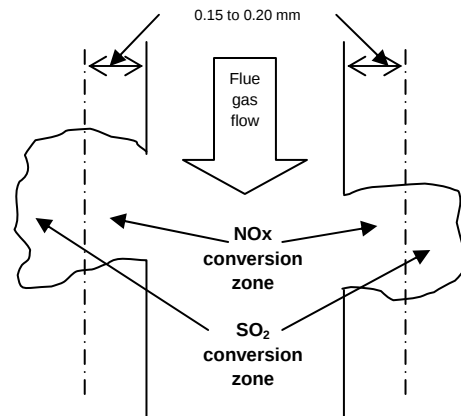


Figure 2: Conversion Zones

To reduce the depth of the pores, OCM's have decreased the wall thickness of the catalyst from original wall thickness of 0.8 to 1.2mm down to 0.6 or less. This has reduced the conversion rate of the catalyst. Early catalyst had a SO_2 to SO_3 conversion rate of between 0.5 to 1%. Today, these have been reduced to 0.2 to 0.3%. There are a lot of variables that effect this rate.

Mercury Oxidation of catalyst

Mercury (Hg) is primarily in the elemental metallic phase (Hg^0) as it is introduced into the boiler. As the flue gas travels through the process, the elemental mercury transitions into oxidized mercury (Hg^{2+}), the bulk of this taking place in the SCR. In its elemental form, mercury (Hg^0) is not easily captured and can be released into the environment as a hazardous substance.

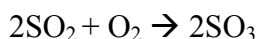
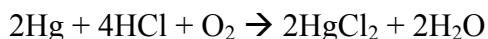
In the SCR, the mercury oxidizes in the vapor phase in the presence of chlorine, yielding a higher potential for mercury oxidation. The oxidized mercury (typically in the form of mercuric chloride- HgCl_2 from the reaction with chlorine inherent in the fuel) is water soluble and can be removed in the FGD. This phenomenon shows a proportional relationship between mercury oxidation and chlorine content.

In the reaction process, ammonia (NH_3) adsorption takes precedence over site chlorination, therefore the NO_x reaction is highly favored over the oxidation of mercury.

Several factors can influence mercury oxidation in the SCR. These can include coal type, halogen content in the coal, SCR temperature, catalyst age and type, and space velocity.

In addition, ammonia adsorption minimizes the coverage of chlorinated sites, thus NOx reduction inhibits Hg oxidation, with both reactions taking place on the surface. In several experiments conducted, it has been observed that at DeNOx rates up to 90%, mercury oxidation greatly occurs. However, beyond 90% DeNOx, oxidation is greatly reduced. Adversely, chlorine content has no effect on DeNOx performance. In ranges from 0-50 ppm, chlorine appears to have the greatest affect on mercury oxidation. Higher temperature ranges enhanced DeNOx potential and reduced mercury oxidation potential while lower temperatures enhance mercury oxidation and lowered DeNOx activity.

In addition to mercury oxidation, SCR catalysts also oxidize sulfur dioxide (SO₂) to sulfur trioxide (SO₃), the precursor to sulfuric acid (H₂SO₄). The correlation between mercury oxidation and SO₂/ SO₃ conversion is close and the reaction mechanisms are as follows:



The reaction of mercury with the HCl and oxygen is considered to be a diffusion-controlled reaction that takes place in the gas phase. The rate of reaction of mercury oxidation is faster than the diffusion velocity of the mercury through the SCR catalyst due to its molecular weight whereas the reaction rate of SO₂ to SO₃ conversion is slower than the diffusion velocity of SO₂ through the catalyst. By altering the catalyst based upon the reaction mechanism, allowing the more active sites to oxidize mercury instead of convert SO₂ to SO₃, higher oxidation rates (>90%) can be achieved while maintaining low conversion rates (< 0.5%).

Catalyst Regeneration

Catalyst rejuvenation / regeneration process has evolved over the last ten (10) years. Evonik was one of the initial organizations involved in the development and commercialization of catalyst rejuvenation / regeneration. The initial years of catalyst rejuvenation / regeneration were focused on the removal of the catalyst poisons and blinding materials from the catalyst and the impregnation of vanadium trioxide (V₂O₃) onto the catalyst.

From 2000 forward, the focus has been on process improvements to increase the longevity of the catalyst and a more thorough understanding of the various reactions to improve the performance of the catalyst. This was required by Evonik to satisfy the demands of Evonik's operating fleet of coal fired units which have over 10,000 m³ of catalyst.

As stated earlier, the OCM used a "homogeneous" material combining all the materials into the catalyst ceramic material including the vanadium. The materials are either applied to the metal substrate and pressed onto the metal substrate ("plate type catalyst"), extruded ("honeycomb type catalyst"), or similar to cardboard manufacture ("corrugated type catalyst").

Evonik's regeneration process utilizes a combination of Evonik held patents, patent pending and licensed technology to rejuvenate and regenerate (impregnation of both vanadium and molybdenum / tungsten) in a single dip process. The vanadium metal is soluble in an acidic (low pH) solution whereas the molybdenum and tungsten are soluble in a basic (high pH) solution.

The original – single dip process for impregnation of the vanadium is to dip the catalyst into a solution and then dry the catalyst.

Utilizing a double dip process has a major disadvantage when working with different pH solutions. The second dip will have the tendency to remove or extract materials from the initial dip, since these materials will want to draw the metals impregnated in the first dip back into the solution. The effectiveness of the material impregnated in the significantly diminished.

In addition to the development activities of Evonik on a single dip process, Evonik has expended significant R&D into the selective impregnation of the various metals (vanadium, molybdenum and/or tungsten) where they provide the optimum performance in the catalyst. The Evonik patent pending process impregnates the vanadium on the surface of the catalyst and to a controlled shallow depth into the catalyst. The molybdenum and/or the tungsten are impregnated into the deeper areas of the pores. (See Figure 2)

The combination of these two Evonik developments provide the advantage of a reduction of the SO_2 to SO_3 conversion rate from 30% to 50% of the original conversion rate of the catalyst while maintaining the same catalyst activity (K_O).

Catalyst Longevity

The catalyst longevity is another consideration for the regeneration process. The impregnation of the molybdenum / tungsten into the deep pore areas of the catalyst material is very critical to maintain the structural integrity of the catalyst.

There are two types of tests for the structural integrity of the catalyst; compressive and bonding (refer to Figure 3). The compressive test is the amount of force applied in the direction of flow. The bonding test is in 90 degrees to the direction of flow.

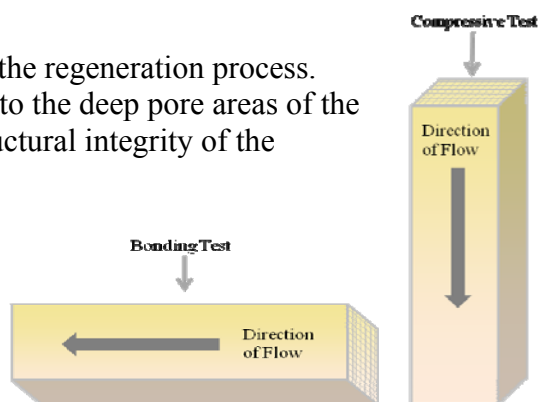


Figure 3: Catalyst Strength Test

There is a separate test for plate type catalyst there is a “drop” test to determine the amount of ceramic material that dislodges from the catalyst metal substrate.

Catalytic material can not only be damaged during the regeneration phase but during removal from the SCR and re-installation, as well as during the transportation from the power plant to the regeneration facility and back. The transportation methodology for “honeycomb” is to transport them in a 90 degree angle to the regular flow direction. Plate and corrugated type catalysts are transported in flow direction. Honeycomb plate will have the greatest stress in the transport at the center of the module as shown in Figure 4. Any type of damage to the honeycomb logs will not be immediately visible, because the bouncing of the “plate” type modules during transport

will force the catalyst material to dislodge from the substructure. The evidence is clearly visible by the small diamonds of catalyst material on the truck bed.

Moisture has a detrimental effect on the catalyst strength. This includes both the surface moisture as well as the inherent or crystalline moisture. During the regeneration process, the strength is reduced by some 50% due to the moisture in the catalyst.

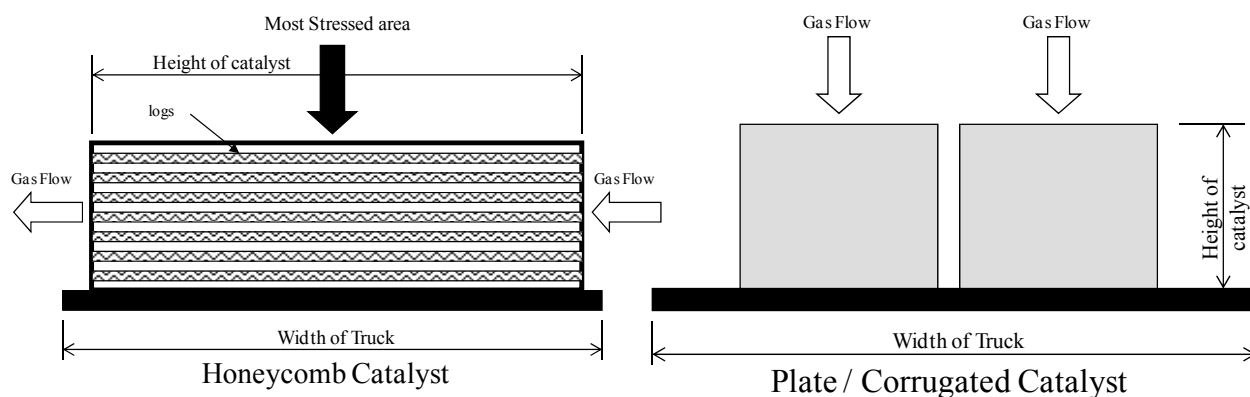


Figure 4: Catalyst Transportation

Re-calcination

Evonik introduced re-calcination to the regeneration market to help improve the longevity of the catalyst and to provide a product which exceeds the original performance of the catalyst. This includes the complete activity replenishment; regain the greatest amount of strength back into the catalyst by removing the water and replenishing the strength materials that are lost during regeneration process. Even the catalyst manufacturer uses calcination in order to (1) strengthen the catalyst by curing/drying the ceramic material by removing both the surface and inherent moisture, (2) bond the strength metals of the catalyst (tungsten / molybdenum) into the catalyst material and (3) reestablish the full activity of the catalyst. It should be noted that the inherent / crystalline water can only be removed at temperatures exceeding 760 °F. Also, the vanadium trioxide (V_2O_3) material needs to be heated above 400 °F to transform the vanadium to a vanadium pentoxide material (V_2O_5).

Similar to calcination of the original catalyst, re-calcination was introduced in the regeneration process by Evonik to perform similar functions as the OCM's. Our research has shown that after regeneration without re-calcination 20 to 50% of the bonding strength is lost. The loss is caused by the reduction of molybdenum and / or tungsten lost in the rejuvenation of the catalyst. Figure 5 shows an actual example of a catalyst that was regenerated without the replenishment of the strength metals. Results after the regeneration showed a loss of 27% of the tungsten material (9% down to 6.5%). There was about an 8% loss in the compressive strength and a 45% loss in the bonding strength. This is honeycomb type of catalyst and the catalyst is not likely to stand another regeneration or transportation cycle.

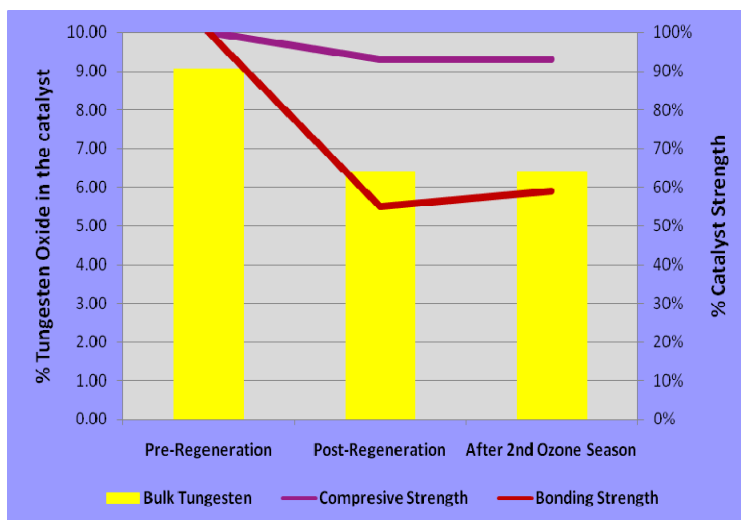


Figure 5: Mechanical Strength Loss

Furthermore, a second set of tests were performed after the 2nd outage season. This test further showed that there was not an increase in strength after operating cycles.

Re-calcination and proper metal impregnation has demonstrated that over 95% of the strength is regained in both directions.

Evonik just finished the 4th regeneration of a layer at Evonik's Bexbach station. This layer had over 100,000 hours of operation prior to this regeneration validating that proper regeneration can provide significant longevity to catalyst. The fourth regeneration was completed and the catalyst was re-installed back into the unit.

The economics of catalyst regeneration are shown in Figure 6. The assumptions are an 18 month outage cycle with a layer replaced during each cycle. The savings are 46% over a new purchase scenario.

	NPV	Estimated Cost
New Catalyst Life Cycle Cost	\$37.6 M	\$57.2 M
Regenerated Life Cycle Cost	\$18.2 M	\$30.5 M
NPV Benefit	\$19.4 M	\$26.7 M

Figure 6: Regeneration Benefit

Conclusions

Catalyst regeneration is a viable process and has been in commercial operation for ten (10) years and is continually improving to provide a product that is the same as a new product with improved SO₂ to SO₃ conversion rate.

It is expected that an SCR will provide a co-benefit by reducing NO_x and oxidizing mercury while minimizing the SO₂ to SO₃ conversion. With faster rates of reaction, simultaneous NO_x reduction and mercury oxidation can occur, provided there is the presence of ammonia. This would tend to equate that the mercury oxidation would occur in the lower elevations of the reactor and the NO_x removal in the upper layers. The reactions for both of these constituents will occur on the outer wall or just in the pores of the catalyst.

The SO₂ to SO₃ conversion occurs in the deeper part of the pores of the catalyst. By minimizing the amount of vanadium pentoxide V₂O₅ at these locations, Evonik has observed that this reaction can be inhibited through actually operating and testing experience. Mercury oxidation within the SCR continues to be studied to quantify the amount of oxidation and identify the exact location where this oxidation occurs. There is a significant amount of R&D and testing being conducted by companies like Southern Company and Evonik as well as the OCM's.

SUMMARY

With annual operation of SCR beginning in 2009 in most of the mid western states and wFGD in 2010, mercury mandates from the various states, and a pending final decision on the outcome of the CAIR and CAMR rulings, the SCR will become a more critical device for multi-emission control.

To minimize the annual operating cost of the SCR with the year round operation, minimizing the catalyst replacement cost will be of a major concern. Regeneration has proven itself as a viable technology and significant cost reduction mechanism. Many utilities are analyzing their fleet SCR requirements including regeneration within their catalyst management strategy.

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