SCR Catalyst Management: Enhancing Operational Flexibility

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Abstract

SCR Catalyst Management is an important consideration for many utilities. Many are focused on the traditional and important considerations related to characterization of the existing catalyst, coordination with outage planning, and basic economic factors. This paper explores the significance of the basic steps as well as key additional operational considerations and technology enhancements and their influence on the catalyst management decision process. Key topics including, the impact of expanded operating temperature range, sensitivity to ammonia:NOx distribution, enhanced NOx reduction efficiency, limitation of SO₃ emissions and enhancement of Hg emissions controls are discussed.

Introduction

Catalyst management refers to a comprehensive methodology for predicting when catalyst layers should be replaced or regenerated, or a new layer added, based on catalyst deactivation rates, performance requirements, and system capabilities. Effective catalyst management requires a long-term plan for maximizing performance based on projected plant outage schedules, future emission regulations, available control technologies, and plant improvements. Catalyst management strategies require evaluation of numerous issues—boiler/SCR system operations, the plant's and fleet's emissions reduction strategy, fuel management, the cost of NO_x credits, outage demands, SO_3 emissions levels, mercury oxidation, capital budget considerations, etc.—with the goal of achieving an optimal solution (Figure 1).

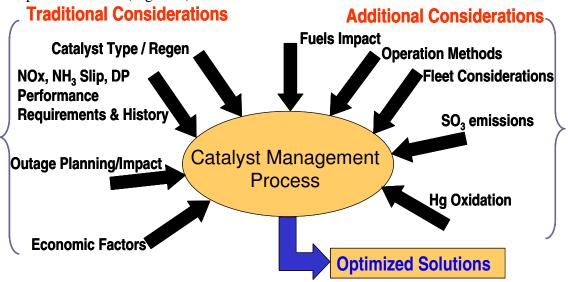
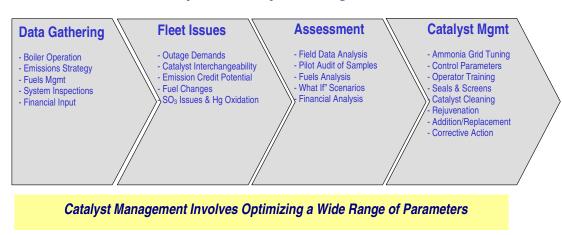


Figure 1. Catalyst Management Considerations

The process can be broken down into specific steps, facilitating its management by the plant owner/operator (Figure 2). Each step must be considered and planned for before determining an optimal solution for the site-specific situation.



Steps in Catalyst Management

Figure 2. Steps in Catalyst Management

Start with an inspection

To optimize the performance of its SCR system, the catalyst's formulation, structure, and volume are designed to take into account key parameters such as:

- Plant performance factors (such as fuel and combustion type, slagging rates, boiler performance, air heater design, particulate collection devices, etc.).
- Operating conditions (flue gas flow rate, inlet NO_x levels, temperature, the impact of O₂ and water content on catalytic potential, etc.).
- System scale-up factors (non-ideal flow distribution, temperature distribution, ammonia-to-NO_x molar ratio distribution, catalyst blockage, etc.).

If any of the above parameters varies from the initial catalyst design conditions, the life of the catalyst may be shortened or extended. The former would be the case if, for example, an SCR system designed to achieve a certain level of NO_x reduction at a given ammonia slip is asked to achieve a higher level of NOx reduction. Conversely, a lower reduction level or a higher allowable ammonia slip would effectively increase the catalyst's useful life.

SCR system inspections and evaluations—which should be performed at least once a year—should include physical inspections of the catalyst, reactor, and ammonia injection system. Field performance data, including inlet NO_x levels, removal efficiency, ammonia-in-ash levels, etc. (as well as operational data such as the number of system starts/stops, operational load range, total hours, fuel data, ash data, etc.) must be collected and compiled to enable proper evaluation of results. Samples of the catalyst should also

be taken to assess its catalytic potential vs. both initial design parameter expectations and actual "as-fired" conditions.

Planning for the future

Until recently, it was possible to manage and evaluate SCR systems in a fairly stable assessment environment. Recently, however, changes in the U.S. generation industry's operating environment have accelerated. The new landscape includes variables such as seasonal market demands, the impact of flue-gas desulfurization system operation, mercury emissions requirements, particulate and opacity limitations, the value of NO_x credits, greater need for cycling operation, fuel variability/flexibility, etc. These issues impact catalyst management both alone and in concert.

One way to assess catalyst activity and measure it against the design deactivation curve is to perform pilot performance tests in a laboratory. Such tests audit the catalytic potential of an SCR catalyst (system and/or layer) by measuring the performance of a field catalyst sample that has been in operation for a known duration. Because the tests are conducted in a controlled environment free from scale-up factors, they allow accurate comparisons of field sample's catalytic potential to that of a fresh catalyst.

The deactivation rate is determined by comparing the change in catalytic potential vs. operating hours of the sample. Measured field performance and characteristics of the fuel fired during the operating period under evaluation are obtained from the plant and used in conjunction with pilot test results to determine the actual unit scale-up factors and assignable causes for measured catalyst potential. This knowledge significantly improves the accuracy of future catalyst performance predictions.

Pilot testing and audits of catalyst activity though laboratory analysis of catalyst samples can provide insight into methods for extending catalyst life. Regular catalyst inspection and sampling can identify potential problems and also provide information on deactivation causes and its prevention. Such tests also provide current data to assess SCR system performance with the flexibility of determining a wide range of "what-if" scenarios. Accordingly, such testing is a required first step in devising an effective catalyst management strategy. Table 1 illustrates some of the tests commonly performed to analyze catalyst activity and predict future catalyst performance.

Test	Analysis objective		
Catalyst Activity Test	Such tests determine the catalyst activity under		
	specific plant or standard conditions utilizing		
	representative size catalyst samples		
	• SO_2/SO_3 conversion rate, Pressure drop Δp ,		
	Initial activity K ₀ , Actual activity K, etc.		
Physical Properties Test	Such tests evaluate physical properties such as		
	catalyst surface area and porosity		
Chemical Composition Test	Such tests evaluate the impact of coal and ash		
	properties on catalyst design and performance.		
	These include tests such as:		
	Electron Spectroscopy for Chemical Analysis		
	(ESCA) that determine catalyst surface		
	chemical composition		
	Semi-Quantitative Spectrographic Analysis that		
	analyzes change in chemical composition.		
	• X-Ray Diffraction that determines the		
	crystalline phase of catalyst may be used in		
	evaluating the chemical composition of		
	catalysts.		

 Table 1: Testing Programs for Measuring & Assessing Catalytic Activity/Potential

A thorough understanding of the specific test conditions avoids producing erroneous or misleading results. Common mistakes include use of inappropriate concentrations of NO_x and SO_x , data evaluation under non-equilibrium conditions, and the use of non-representative samples. The European VGB guideline attempts to address some of these issues. However, because specific supplements are still required to achieve valid test results, turning to a qualified laboratory and/or service providers is essential to ensuring a proper evaluation.

Analyzing the data

Variations in fuel characteristics can have a considerable impact on catalyst life. The nature of the fuel fired (be it Powder River Basin or eastern bituminous coal, petcoke, or blends of both) will dictate in large part the rate of catalyst deactivation. Historical data and know-how are key to an accurate assessment of what to expect in the future. Analytic tools such as the one shown in Figure 3 are invaluable in assessing a fuel's impact on a catalyst's long-term effectiveness.

Once catalyst testing and data evaluation are complete, the catalyst's activity potential is assessed in combination with field data and the future operating considerations described in the previous section; the goal here is to determine the available catalyst-management

options. Figure 4 is an example of a catalyst management plan that can take into account a wide range of influences on catalyst management decisions.

Generally, there are three catalyst-management options that may be used alone or in combination: system optimization, catalyst addition/replacement, and catalyst rejuvenation.

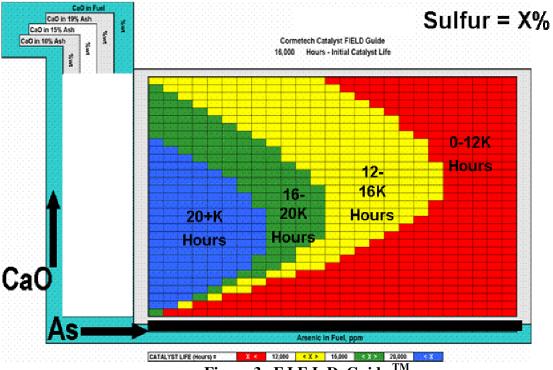


Figure 3. F.I.E.L.D. Guide TM

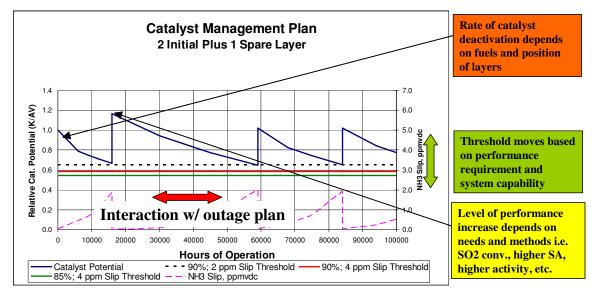


Figure 4. Catalyst Management Plan

System optimization

The purpose of ammonia injection grid (AIG) tuning is to ensure an even ammonia- NO_x molar ratio distribution to the catalyst. Contrary to popular belief, the goal of doing so is not necessarily to get the outlet NO_x profile flat; this is possible only when the inlet profile is flat. If the inlet profile is skewed, there are generally two options:

- Tune the AIG to match the inlet distribution over the load range. In this case, the outlet NO_x profile will not necessarily be flat.
- Attempt to flatten the distribution through mixing technology.

The level of AIG tuning will depend upon the system design and operational methodology. Proper AIG tuning/NH₃:NO_x distribution ensures maximum system efficiency and reduced ammonia slip and can effectively extend catalyst life. The process also eliminates localized regions of high ammonia slip, which can lead to air preheater fouling when combined with SO₃. Evaluation tools such as that shown in Figure 5 are utilized to evaluate the impact of varying NH₃:NOx distribution on local slip and maximum removal efficiency capability.

Specific tests can be conducted to facilitate tuning the AIG until it is operating at peak performance. Periodic checking and optimization of the ammonia-to- NO_x distribution are essential for ensuring the long-term optimal performance of an SCR system. The frequency of tuning is dictated by unit-specific conditions, including NO_x distribution from the boiler and the style of AIG/mixer system in use. In general, it is worthwhile to check the distribution annually.

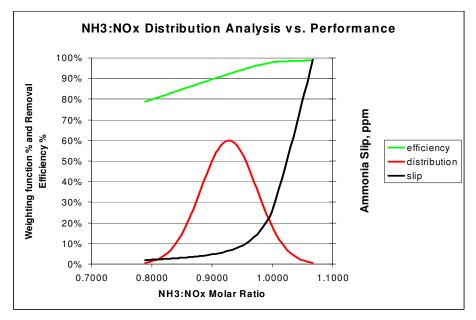


Figure 5. Evaluation of NH₃:NOx Distribution

Flow modeling and catalyst operating limitations are also important aspects in the initial design of an SCR system. Over time, these considerations may influence the performance life, range of operation, and effective cost of the system. Specific areas where additional testing and/or evaluation may be warranted for system optimization include:

- Testing for expansion of operating temperature range to allow use of the SCR at lower loads, thus avoiding the cost associated with "lost" NO_x reduction.
- Flow modeling for evaluation of LPA (large-particle ash) mitigation methods.
- Flow modeling for AIG/mixing optimization.

Catalyst Addition or Replacement

The key to managing catalysts effectively is to determine an optimum catalyst replacement/addition plan (i.e., when a catalyst should be replaced or an additional layer added). As discussed, the key factors of this assessment include performance audits that analyze the remaining potential of the catalyst. The remaining life of the field catalyst, analyzed in conjunction with the operating history and projected use of the SCR, outage schedule and economic/financial factors, are used to decide what catalyst action should take place.

In most cases, SCR catalyst reactors were built with at least one spare layer. Utilization of this layer generally results in the best economic option for utilities due to the significant life benefit provided, vs. removing and regenerating a layer. Therefore, for most utilities catalyst additions will be the first action followed by replacements or rejuvenation. Because catalyst layers will deactivate at different rates depending upon the fuel fired, the information dictating which layer should be replaced will be generated from the performance audit, which may also be potentially applied to other fleet units considered at the time.

An important step to include in this decision process is associated with catalyst advancements available at the time of need. For example, in units that have either a large pitch or a short catalyst length, there is substantial opportunity to improve the performance potential of the unit. This may be important when considering issues such as the value of eliminating the cost associated with an SCR catalyst action during a planned outage, generating NO_x credits, and—in some cases—meeting a mercury emissions-reduction goal.

Transitioning to an alternate product can be done in a staged and qualified manner to minimize any risk of a wholesale change in the catalyst. Alternately, this method may be used to reduce the cost of the purchased catalyst by taking advantage of the performance benefit through reduced volume. In either case, catalyst advancements should be an integral part of the management planning process. In some cases, they can provide more than a 50% performance enhancement or cost reduction, compared to installing a new layer of the original catalyst.

Case in point: the TVA Allen Plant represented a unique challenge for catalyst management due to its two layer catalyst limitation and because the units were built without an SCR bypass, thereby operating on a year-round basis. The units started with an 8.2 mm pitch Cormetech honeycomb catalyst. Keeping in mind potential future use and resulting catalyst management cost savings, the 7 mm product was also qualified during the initial design and installation. In the second year of service, after approximately 16,000 hours of operation, catalyst life-cycle planning was required. Numerous options were investigated ranging from in-kind replacement to insitu washing, external washing, and rejuvenation. The solution involved an in-situ replacement (patent pending) of the 8.2 mm pitch product with an extension of the pre-qualified 7 mm pitch product (patent pending). The same process has been successfully carried out on all 3 units over the last 18 months.

Rejuvenating a catalyst

Cleaning can be a highly effective catalyst performance recovery method in plants where excessive accumulation of particulate matter is affecting emissions performance and increasing draft loss. Cleaning refers to removal of physical restrictions due to buildup of LPA or popcorn ash, and/or flyash that blocks flue-gas access to the catalyst surface. Cleaning methods can be dry or make use of an aqueous solution. Cleaning may be done in-situ, on-site, or off-site.

The dry method of cleaning typically involves a combination of vacuuming and air lancing to remove the ash from the reactor; in gas applications, it also may include removal of insulation debris and/or rust scale. This process is typically very effective where the modules have flyash buildup but no LPA in the catalyst. This can be performed in-situ or off-site, depending on site logistics and outage considerations.

Wet cleaning of severe ash buildup on a catalyst cleaning is referred to as washing, regeneration, or rejuvenation, depending upon the process and aqueous solution used. This is a more elaborate cleaning process that removes most of the chemical buildup on the catalyst surface. The process generally restores the catalyst activity lost to both gross and fine physical blockage. In addition, the process can be used to restore all or a portion of the catalytic activity lost due to chemical poisons.

Generally, the regeneration process consists of the following steps:

- 1. Baseline testing of the catalyst to assess performance recovery.
- 2. Blowing and vacuuming ash off the catalyst.
- 3. Adding ultrasonic energy, bubbling air in the solution and/or physically moving the module to remove any remaining ash.
- 4. Washing the catalyst module using a cleansing solution. This may need to be done multiple times, with different solutions, in accordance with the system vendor's recommendations.
- 5. Drying each catalyst module using forced hot air.
- 6. Testing the catalyst elements to verify that the cleaning has met the established goals.

Regeneration/cleaning must be considered at every plant where the condition of the catalyst condition and its remaining service life dictate it. If it is determined to be economically advantageous to the plant, catalyst cleaning can extend the active life span of a catalyst and be an essential part of a catalyst management program for a plant. In all cases, the process should be pre-qualified on samples prior to implementation of the full-scale process. Items for consideration include the level of activity recovery (physical or chemical), the impacts on SO₂ conversion and mercury oxidation, cost, schedule, and any applicable warranty conditions.

Key Additional Considerations

There are many additional considerations involved in the process of catalyst management. Many are utility, plant specific, and/or unit specific. Three topics of particular significance are 1) Expansion of allowable operating temperature range, 2) Hg oxidation, and 3) Limitation of SO₃ emissions.

1) Expansion of allowable operating temperature range – Traditional techniques for dealing with low temperature operation of SCR catalyst include a) load limiting i.e. restrict unit operation to a load which maintains SCR inlet temperature above Ammonia BiSulfate (ABS) formation, b) Install and utilize flue gas temperature control i.e. burner, gas-side bypass, or water side bypass.

The temperature at which ABS forms is a function of the concentration of water vapor, SO_3 and NH_3 . Under the proper conditions ABS will condense in the catalyst pores masking of active catalytic sites, thus limiting SCR catalyst potential to reduce NOx (Figure 6).

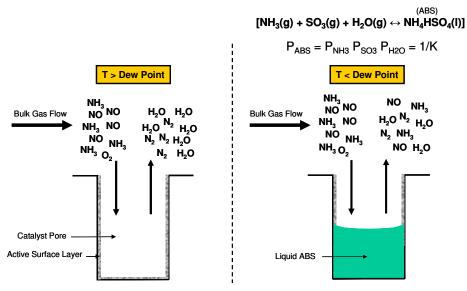


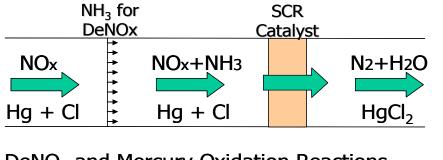
Figure 6. Pore Condensation of ABS

Many units installed economizer bypass systems to maintain SCR inlet temperature, others evaluated the associated capital, operating, and maintenance expense and decided to increase the minimum load specification in order to maintain temperature. Both of which can present either direct or indirect expense to the utility.

Based on a need presented to by one of it's customers to expand the operating temperature range of their SCR, Cormetech focused on phenomenon which restricted operation, namely formation of ABS in the catalyst, and methods to assess performance impacts and risks. Subsequent to this investigation, it was found that many utility clients had a need/desire to expand the operating temperature range of the SCR to take advantage of generation of generation of NOx credits and/or reduction NOx emitted against a cap. Based on this need, Cormetech continued fundamental work in this area to expand the capability to advise clients on optimizing the SCR operating range.

The basic process includes an understanding of the catalyst performance as a function of its available catalyst pore structure, principles of pore condensation, and boiler operational goals in terms of NOx reduction and time, as well as the limitations, including SO₃ emissions, recovery temperature, ramp rate, control logic options, etc. Results from specific investigations have generated significant savings (> \$2MM annually) related to the value of NOx and or allowed more effective utilization of system wide generating units.

2) *Hg Oxidation* – SCR catalyst will oxidize mercury to varying degrees based on a wide variety of inputs including catalyst type, NH_3 concentration, temperature, HCl concentration, etc. The basic reaction process is described in Figure 7.



Denox and Mercury	<u> Oxidation Reaction</u>		<u>15</u>	
NO + NH ₃ + 1/4 O ₂ \rightarrow N ₂	+ 3/2 H ₂ O	(NO _x	Reduction)	

100 + 1013 + 174 02	$2 H_2 + 0/2 H_2 0$	(NO _x riculation)
Hg + 2 HCl + $\frac{1}{2}O_2 \rightarrow$	HgCl ₂ + H ₂ O	(Hg Oxidation)
$HgCl_2 + NH_3 + {}^{1}\!\!/_4 \operatorname{O}_2 \ \not \rightarrow \\$	Hg + 2 HCl + $\frac{1}{2}$ N ₂ + $\frac{1}{2}$ H ₂ O	(HgCl ₂ Reduction)

Figure 7. General SCR Chemistry for Hg Oxidation

Use of the SCR in combination with a wet Flue Gas Desulfurization (FGD) system can be an effective method for meeting Hg emission limits. Cormetech has worked with

industry partners, EPA, and utilities over the last 3 to 4 years to develop and demonstrate know-how related to predicting and guaranteeing the level of Hg oxidation through it's SCR catalyst. Figure 8 shows an example of actual field performance versus predictive models for aged SCR catalyst.

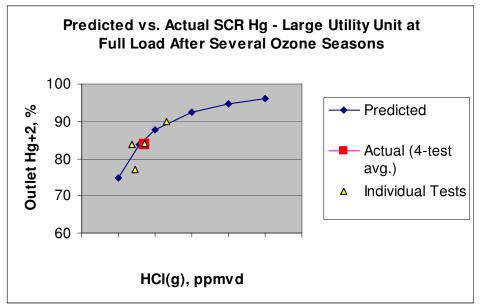


Figure 8. Full Scale Hg Oxidation Results on Aged SCR Catalyst

Use of information developed to date regarding Hg oxidation capabilities will be combined with the more traditional SCR catalyst management decision making process as outlined in figure 4 to assist utilities to optimize catalyst management.

3) Limitation of SO_3 emissions - Historically, minimizing SO_2 conversion while maintaining high levels of NOx reduction were in conflict, and in some cases could not be achieved. Therefore, Cormetech focused on developing additional catalyst product features to minimize SO_2 conversion while maintaining high catalyst activity yielding high NOx reduction capability with low ammonia slip. The product extension utilizes advanced extrusion, product and materials know-how in combination with a well proven product base. The performance enhancement can, in some cases, achieve less than 0.1% SO_2 oxidation while maintaining all other key product performance and durability features. Use of the advanced SCR product may be exclusive or combined with other SO_3 mitigation techniques including; fuel switching, in-furnace mitigation with reagent, and pre/post APH mitigation with reagent.

The superior performance of the low SO_2 conversion catalyst relative to a conventional catalyst is because of greater open area, thinner wall thickness, improved composition and geometry for strength. The design is optimized to reduce volume, pressure drop and SO_2 oxidation rate. Table 2 outlines some of the performance characteristics of the new product in comparison to the conventional catalyst in terms of relative catalyst volume,

pressure drop and SO_2 oxidation. Two cases are shown to illustrate the alternative methods for utilizing the features of the high open are product.

	Product			Case 1		Case 2	
							Relative
				Relative	Relative	Relative	SO2
		Opening	GSA	Volume	Pressure	Volume	Oxidation
Product	Pitch	(mm)	(m2/m3)	Required	Drop	Required	Required
Conventional	7.4	6.3	445	100%	100%	100%	100%
High							
Performance	6.9	6.3	539	75%	61%	100%	25%

Table 2: Advanced SO₂ Conversion Catalyst Performance Summary

Initial installations of Cormetech's low SO₂ conversion catalysts at full reactors with < 0.5% SO₂ conversion were designed in 2002 and installed in 2003 and continue to operate successfully. Subsequent individual layer additions of the low SO₂ conversion catalyst have been designed and installed with conversion rates of less than 0.1%. A base installation exceeding 40,000 MW of coal fired units in the U.S. utilize a form of the high open area/high performance product. An additional 5,500 MW, 2,000MW of which are in operation are applying another extension of the technology to achieve greater overall SCR performance at lower SO₂ conversion.

Conclusion

SCR Catalyst Management presents a diverse and complex issue for many utilities. The US industry is now approaching the time in which significant catalyst management decisions will be made as layer additions/replacements and new installations are required in order to maintain performance and/or achieve new regulatory challenges. The SCR catalyst and system has a significant impact beyond just NOx reduction which must be considered in the decision making process. Cormetech has unique knowledge and capability to assist utilities to evaluate and optimize the SCR catalyst management process to achieve performance goals in NOx reduction, Hg oxidation, SO₃ emissions, and operation flexibility.

Key Words

Selective catalytic reduction, catalyst management, SO₃, mercury oxidation, operating range, AIG tuning.

Related Papers/Articles

Power Magazine Vol 150 No. 1 – Long Term Catalyst Healthcare Power Engineering Magazine May 2006 – Improved Catalyst can Clean the Air ICAC Conference 2005 - Effects of SCR Catalyst and Wet FGD Additive on the Speciation and Removal of Mercury within a Forced-Oxidized Limestone Scrubber