SCR Catalyst Management

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Abstract

Selective Catalytic Reduction, SCR, is recognized worldwide as the most effective control technology of Nitrogen Oxides or NOx. SCR catalyst is applied to utility boilers and combustion turbines when substantial NOx reduction of 50% to 95% is required.

SCR system capabilities and performance requirements, as well as SCR catalyst deactivation rates, are vital to forecasting when SCR catalyst layers should be replaced or regenerated, or a new layer added. This is the essence of catalyst management

The key to managing catalysts effectively is to determine an optimum plan for catalyst replacement or addition. Traditional tools are available to the customer for developing an effective catalyst management strategy. They include performance audits that analyze the remaining potential of the catalyst with plant operating history, projected use of the SCR, fuels used, the position of catalyst layers, outage schedules, economic/financial factors and analysis of recent catalyst technology advancements. Considerations such as low-load operation

flexibility, mercury (Hg) oxidation and lower SO_3 emissions are becoming critical when developing a comprehensive catalyst management program.

This paper will serve to be an experience based, knowledge driven commentary of SCR catalyst and the many benefits associated with this technology. Documentation of current management practices will be provided and technological advancements of the product and procedures that encompass the reduction of NOx emissions from stationary sources burning fossil fuels using SCR catalyst will be elucidated.

Background

SCR technology was first applied on utility boilers in the 1970s in Japan. Later introduced in Europe during the 1980s, the first large power plant equipped with SCR in Germany began operating in December 1985 on a 460 Megawatt unit. By 1990, the number of commercial units in Japan and Germany had grown to about 200 units or about 40,000 MW of capacity. Three-fourths of West Germany's entire utility generating capacity was utilizing SCR by the end of 1992. Most applications in Japan and Germany were designed to achieve 60%-80% NO_x removal efficiencies. In Austria, which proposed Europe's most stringent NO_x regulations early on, a full-scale SCR pilot plant began operation in 1985. Austrian utilities began retrofitting SCR systems in 1986.

The United States was the third major region to implement Selective Catalytic Reduction (SCR) technology on coal fired utility boiler applications, after Japan and Europe. Several SCRs were installed in the US in the early/mid 1990s, and the majority of the SCR currently in operation in the US were installed between 1999 and 2006. Utilities are continuing to retrofit existing boilers with SCR as well as installing SCR on new boilers that are currently in construction. There are many aspects of operation of SCR in the US that differ from the historical experience; this includes regulatory drivers, fuels and owner/operators' approaches to meeting emissions goals.

At present there is more than 110,000 MW of capacity in the United States that utilize this revolutionary technology to control NO_x emissions.

Process Overview - Chemistry

Selective Catalytic Reduction (SCR) is a process which reduces the concentration of nitrogen oxides (NO_X) by means of chemical reactions in the presence of a catalyst. SCR systems are used primarily to treat the exhaust gas of large stationary combustion sources, but have been used in many other applications where fuel is combusted as a source.

The primary SCR reaction is $4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$ (or $NO + NO_2 + 2NH_3 \rightarrow 2N_2 + 3H_2O$).

The reactants are NO_X, which is present in the flue gas in the form of nitrogen oxide (NO) and nitrogen dioxide (NO_2), and oxygen (O_2). Ammonia (NH_3) is injected into the flue gas stream independent from the combustion process via a part of the SCR system, the Ammonia Injection Grid (AIG). In some cases, urea (CON_2H_4) is used as a substitute for NH_3, but it is typically converted to NH_3 before it reacts with NO_X.

The products of the SCR reaction are nitrogen (N_2) and water (H_2O). There will also be some residual NO_X and NH_3 which were not reacted but the amount of residual NO_X is determined by the required removal efficiency of the SCR. Similarly, the amount of residual NH_3, referred to as ammonia slip, will be set according to project requirements.

An undesirable reaction that occurs in the SCR catalyst process would be is the SO_2 oxidation reaction:

$$SO_2 + \frac{1}{2} O_2 \rightarrow SO_3$$

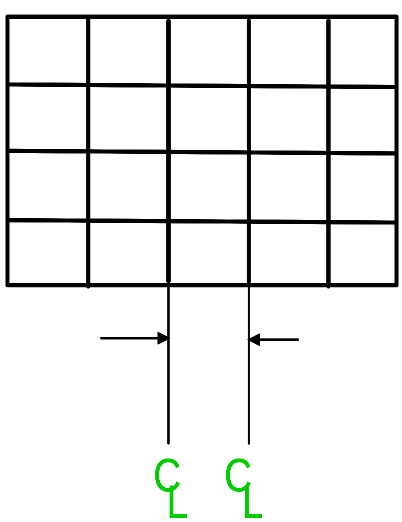
This resultant increase in SO_3 can be detrimental to downstream equipment through the formation of, H_2SO_4 (sulfuric acid) and, when combined with ammonia, ammonia bisulfate (NH_4HSO_4).

These reactions take place in the presence of the SCR catalyst. Like all catalysts, the SCR catalyst encourages chemical reactions to occur, but it is neither consumed nor produced by these reactions. However, the catalyst will degrade over time due to contaminants in the exhaust gases and exposure to various operating conditions.

SCR Catalyst Design Parameters

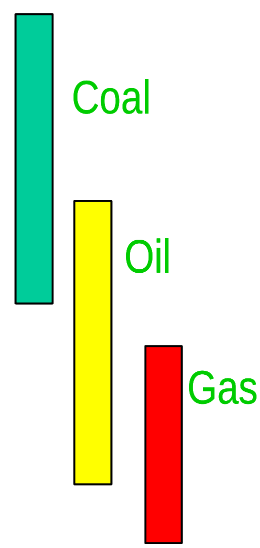
The determination of the appropriate catalyst structure and size is an initial determining factor in the design of a SCR system. There are three variations on a theme when considering SCR catalyst selection. This paper will focus on honeycomb catalyst, an extruded ceramic monolith with high surface area. The two other forms of SCR catalyst are both coated plate type products, the difference being the substrate to which the coating adheres.

Determination of size or pitch (the measurement from the mid-line of the cell wall to the mid-line of adjoining cell wall) is based first on fuel type for honeycomb catalyst. Honeycomb SCR catalyst is custom designed for situational combustion products such as but not limited to coal, natural gas, or oil.



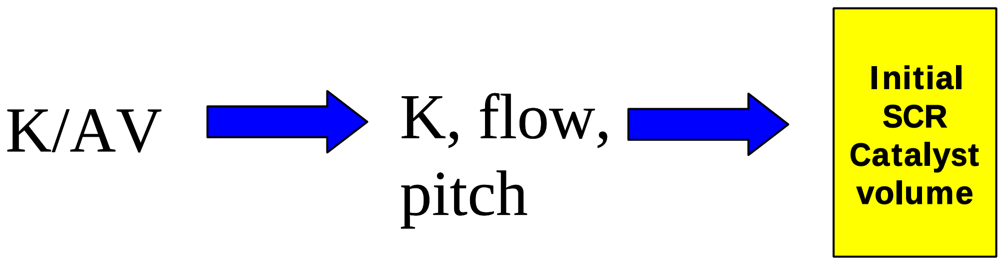
Pitch

- 9.2 mm = 16 cell
- 8.2 mm = 18 cell
- 7.4 mm = 20 cell
- 7.1 mm = 21 cell
- 6.9 mm = 22 cell
- 6.4 mm = 23 cell
- 5.9 mm = 25 cell
- 4.2 mm = 35 cell
- 3.7 mm = 40 cell
- 3.3 mm = 45 cell
- 2.7 mm = 55 cell = 87 cpsi
- 2.1 mm = 70 cell = 140 cpsi

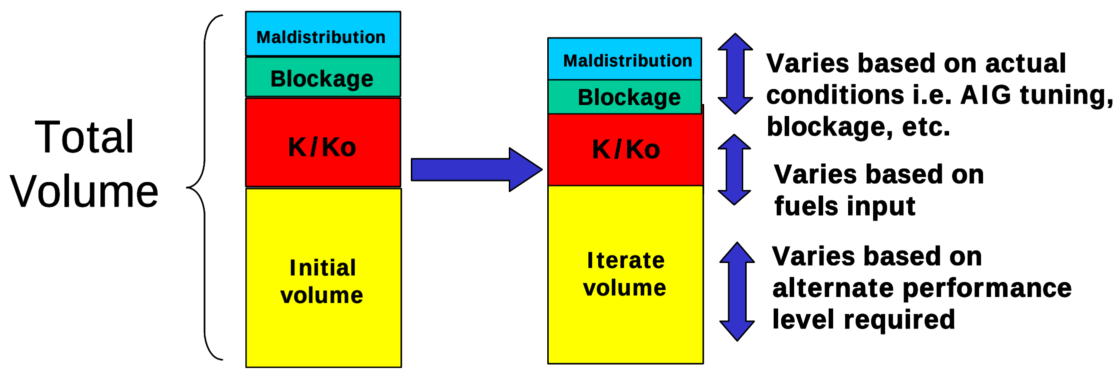


Acknowledging the initial conclusion, designing for the customer specifications requires more information to specifically target the correct formulation of the catalyst.

Specific design parameters are next in the evaluation that include determining minimum catalyst potential requirement, determining initial catalyst activity, and volumetric gas flow in order to solve for an initial first catalyst volume.



Going further into the design algorithm, the next determination would be the margin required for fuels, blockage of catalyst cells due to obstruction, and maldistribution. Once discovered, the design engineer will iterate solutions based on margin impact on formulation and activity.



The goal of this process is optimal performance, a custom tailored SCR catalyst design that will not only meet, but exceed customer expectations.

SCR System Design

Coal-fired SCR designs incorporate multiple layers of catalyst. The initial catalyst volume requirements for large-scale coal-fired SCR applications typically exceed the catalyst volume that can be manufactured in a single layer.

Multiple layer SCR designs provide flexibility in managing the life of the SCR catalyst and the performance of the SCR system. In cases where a single layer of catalyst can meet the initial performance requirements, a coal-fired SCR reactor design should include provisions for at least one additional layer.

Experience has shown that the most oft utilized coal-fired SCR reactor arrangement consists of two initial layers plus one future layer (2 + 1). Less common but still within experience are SCR reactor arrangements consisting of various catalyst layer arrangements.

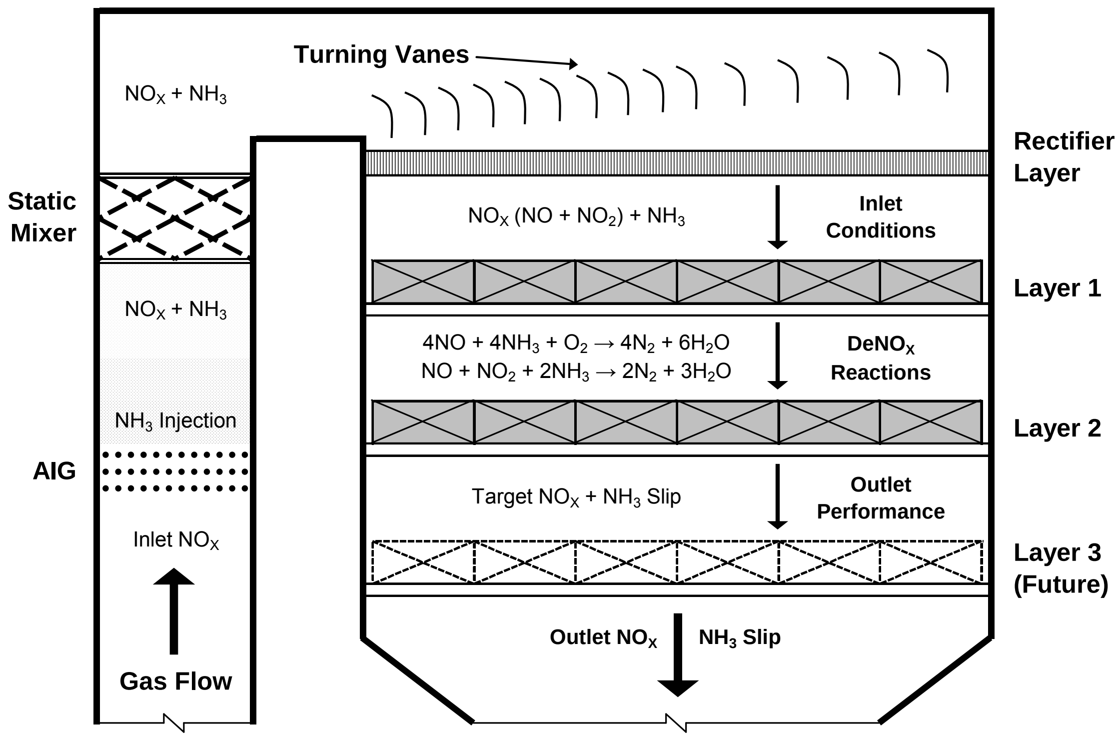


Figure 1 Typical SCR Reactor Arrangement (2+1 Layer)

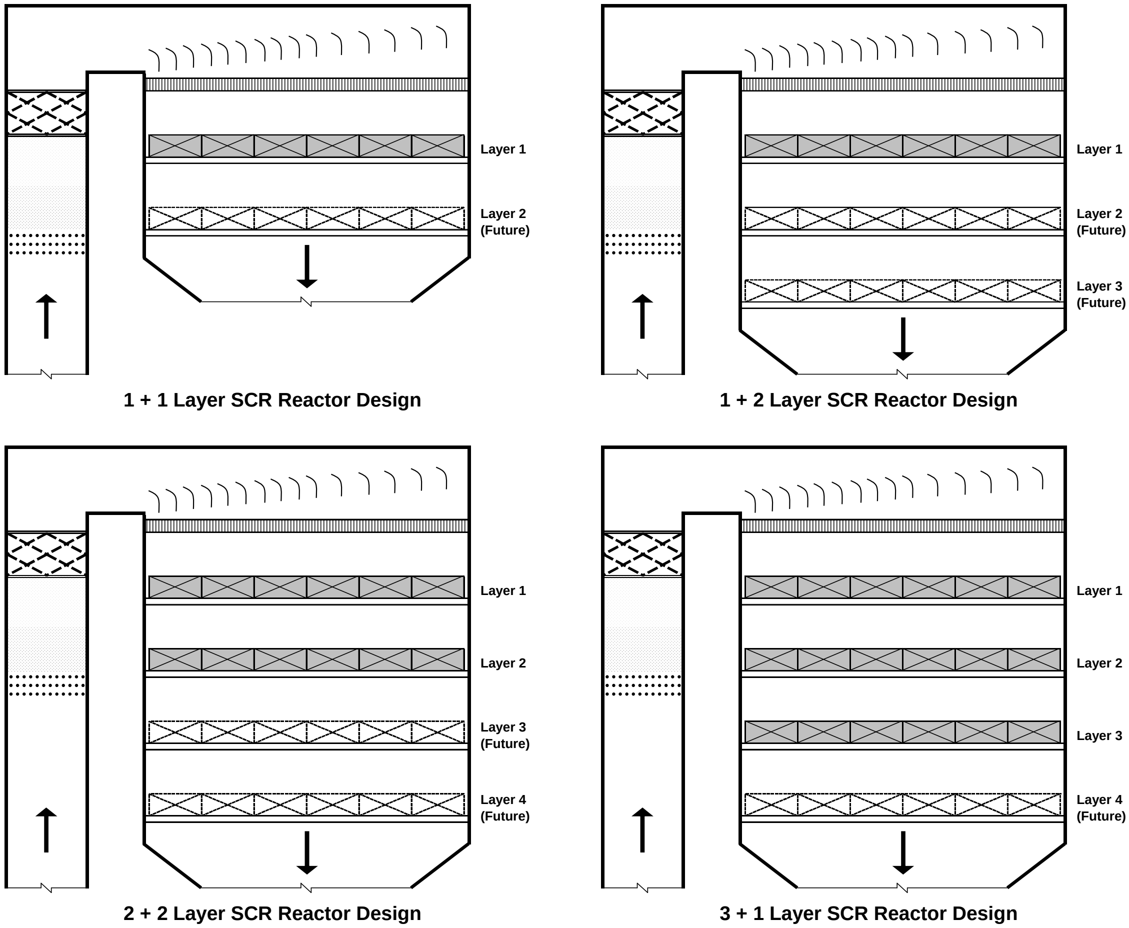


Figure 2 Alternate SCR Reactor Arrangements

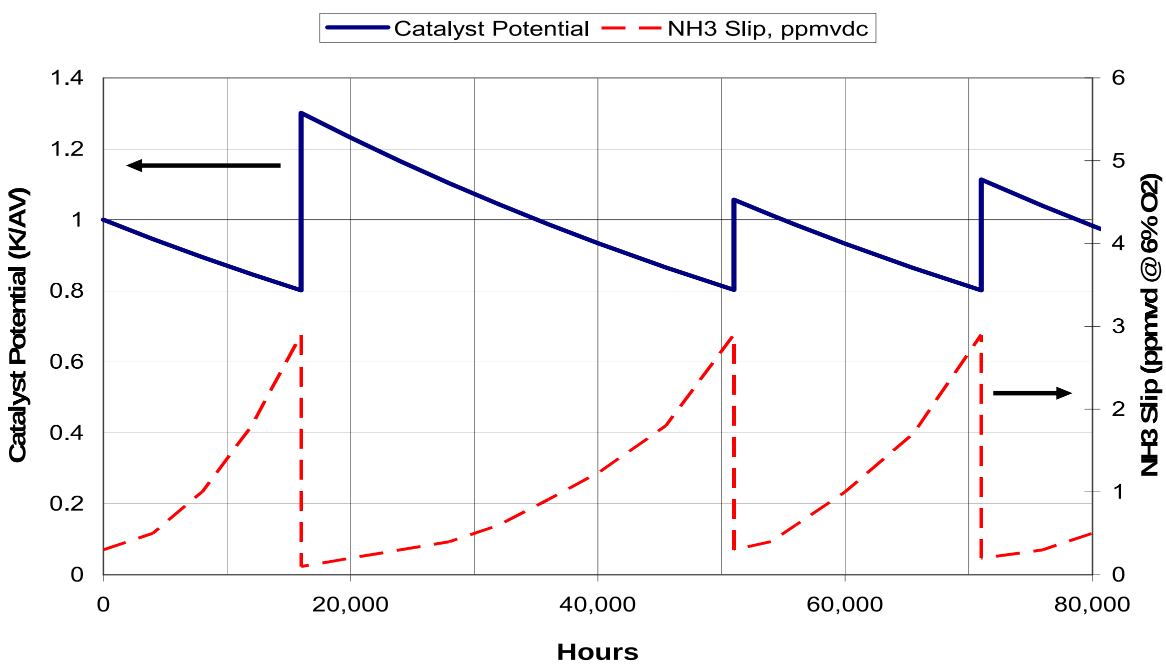
Compared to gas- or oil-fired units, coal-fired SCR units require relatively high catalyst volumes. Experience from multiple SCR catalyst installations show an SCR projects average installation quantities provided are approximately 0.75 cubic meters of catalyst per megawatt. A typical SCR application for a 1,000 MW boiler would likely require about 750 m^3 of catalyst.

Once the combustion gases begin to flow through the SCR reactor the catalyst will begin to deactivate. Over time, the catalytic potential will decrease and eventually fail to provide the required deNO_X performance. The rate of catalyst deactivation is dependent on the fuel that is fired in the boiler. The deactivation rates for different coals can vary widely, and can be relatively severe in some cases. The catalyst supplier will consider the coal and ash analysis provided by the customer during the design phase and account for the expected deactivation rate during the guarantee period.

The combination of relatively high catalyst volumes and significant deactivation potential for coal-fired SCR applications should encourage utilities to maximize the value of their investments in SCR catalyst. Effective utilization of layer additions and catalyst management techniques can help utilities achieve this goal.

Catalyst Management

SCR catalyst is designed to provide a level of performance for a specified period of time. A timeframe of 8,000 – 24,000 hours is considered typical. Once the SCR catalyst has reached the end of the design life, catalyst layer addition or replacement is required in order for the SCR to maintain performance. Proper catalyst management enables the owner to optimize the value and performance of the SCR catalyst over the life of the SCR system. A catalyst management plan is a useful tool for understanding the expected catalyst performance and planning for activities such as catalyst layer addition, replacement, or regeneration.



`**Figure 3 Catalyst Management Plan** 16,000 Hour Design Life (2 + 1 Layer)

The left axis of the management plan represents the relative catalyst potential, which starts with a value of 1.0 and decreases over time based on the deactivation rate of the catalyst. The deactivation rate depends on the characteristics of the coals that are fired in the boiler.

The right axis of the management plan represents the NH_3 slip. The NH_3 slip typically starts at a very low level and increases gradually as the catalyst deactivates. The NH_3 slip will reach the design limit when the catalyst has deactivated to the minimum acceptable potential. This should also coincide with the design life of the catalyst.

At this point, the management plan calls for adding a catalyst layer. Catalyst potential increases significantly, and the NH_3 slip returns to a low level. The catalyst continues to deactivate, and when the catalyst potential reaches the minimum acceptable level again, the first catalyst layer replacement should occur. Catalyst layer replacements continue throughout the life of the SCR system.

The catalyst management plan shown in Figure 3 is constructed based on the assumption that each future catalyst layer addition and replacement will provide the same catalyst potential as one original catalyst layer. This is easily seen in the impact of the first layer addition. The original relative catalyst potential is 1.0. At the end of guarantee period (16,000 hours), the catalyst potential has decreased to 0.8. This indicates that 80 percent of the original catalyst potential remains, and that 20 percent of the original catalyst potential is expected to deactivate. When the third layer of catalyst is added, the relative catalyst potential will increase to 1.3. Therefore, the relative catalyst potential of the layer addition is 0.5, which is equal to half (one layer) of the original catalyst.

It is convenient to assume that all catalyst layers will be identical when calculating the initial catalyst management plan. However, it is not necessary for a utility to keep all catalyst layers within a reactor the same. In many cases, catalyst layer additions and replacements will be different from the original catalyst layers. There are several reasons for the owner to prefer a catalyst layer that is not the same as the installed catalyst.

At the end of the design life for the original SCR catalyst, the performance requirements for the SCR system may be adjusted. Some owners may want to minimize the additional SO_2 conversion or the pressure drop of a layer addition. This may result in selecting a lower activity catalyst, a smaller volume, or a different pitch catalyst for the layer addition. Product advancements may result in the utility selecting a different type of catalyst for the layer addition. The layer addition process provides the owner and the catalyst supplier a key opportunity. The performance of the existing catalyst and design the catalyst layer addition to meet the future requirements of the system can be evaluated and enhanced.

Catalyst Layer Addition

There are two general methods of specifying catalyst layer additions. The first approach is based on maintaining the performance of the existing SCR system and providing some associated performance guarantees. The second approach is based solely on the physical and chemical characteristics of the catalyst layer addition. In either of the catalyst specification methods, the specification should also include the information described in Table 1.

Site Specific SCR System Information		
a.	Reactor drawings specific to catalyst module / support beam interface	
b.	Product feature preferences [catalyst pitch, opening size, etc.]	
c.	Operating limitations [pressure drop, SO_2 oxidation, etc.]	
d.	Coal and ash specifications	
e.	Anticipated future changes to operation or fuels	
f.	SCR process conditions	
	i.	Gas flow rate
	ii.	Temperature
	iii.	Inlet NO_X
	iv.	Inlet SO_2
	v.	Inlet SO_3
	vi.	H_2O
	vii.	O_2

Table 1 Site Specific Information Required for Catalyst Layer Additions

Note that when a layer of catalyst is added to the SCR system, the total pressure drop and SO_2 conversion rate will increase. The amount of increase can be controlled to some extent through the design of the catalyst layer.

System Performance Approach

In the system performance approach, the performance requirements specified are similar to those that were specified with the original SCR project (deNO$_X$ efficiency, ammonia slip). The catalyst layer addition will be operated in conjunction with the existing installed catalyst and the effectiveness of the overall SCR system is dependent upon the joint performance of the existing catalyst and the new catalyst. This is relatively straightforward if the original (OEM) catalyst supplier will also supply the layer addition.

In order for a different (non-OEM) catalyst supplier to provide a design and offer commercial guarantees under this methodology, they must have significant knowledge related to the design of the original catalyst. It is possible that the owner utility does not have access to this level of design detail.

Table 2 provides a summary of information that the owner should include in the specification of catalyst layer additions when system-based performance guarantees are required. The OEM catalyst supplier will already have most of the required information based on the original design. If non-OEM catalyst suppliers are invited to bid on the catalyst layer addition, the owner will need to provide more extensive information regarding the existing catalyst design and performance. This data will allow non-OEM suppliers to calculate the catalyst potential (K/AV) and understand the rate of catalyst deactivation, ultimately allowing the supplier to offer commercial guarantees associated with the overall SCR performance.

The catalyst supplier offers may include caveats associated with the condition of the original catalyst at the end of the new lifetime. For example, they may require that the K/AV of the original catalyst be ≥ X at the end of the new guarantee period. Similarly, there may be conditions associated with the rate of catalyst deactivation, which is typically considered to be same as historical. If this is not the case, coal and ash analysis data will be required in order to predict the deactivation rate and determine the performance lifetime of the system.

System Performance Approach			
a.	Similar performance requirements as original procurement		
	i.	$DeNO_X$ efficiency	
	ii.	NH_3 slip	
	iii.	Catalyst life	
	iv.	Catalyst pressure drop	
	v.	SO_2 oxidation	
b.	Additional information regarding existing catalyst required for non-OEM catalyst suppliers to offer system performance guarantees		
	i.	Original catalyst volume	
	ii.	Original catalyst geometric surface area [m^2 / m^3]	
	iii.	Original catalyst activity [Ko]	
		1.	Activity test conditions [AV, Temperature, NH_3:NO_X MR]
	iv.	Original catalyst current activity [Ke]	
	v.	Age of catalyst [operating hours]	
	vi.	Reactor location of the new catalyst layer [1st, 2nd, 3rd, etc.]	
	vii.	Catalyst inlet conditions	
		1.	NH_3:NO_X [+/- %RMS]
		2.	Velocity [+/- %RMS]
		3.	Temperature [+/- °C]

Table 2 System Performance Specification Data

Catalyst Product Specification Approach

The second approach is a product type guarantee for the single layer. The catalyst is evaluated on the basis of catalyst activity, surface area and SO_2 oxidation rate for the single layer. The utility manages the performance associated with the integration of the new layer with the existing layers installed to assure that the $deNO_X$, ammonia slip and life goals are achieved. In this case, the utility specifies the minimum catalytic potential of the layer being procured. Typical requirements for this type of specification are provided in Table 3.

Catalyst Product Specification Approach
a. Typical catalyst specifications for the layer addition or replacement
i. Catalyst pitch
ii. Catalyst geometric surface area [m^2 / m^3]
iii. Catalyst initial activity [Ko]
1. Activity test conditions [AV, Temperature, NH_3:NO_X MR]
iv. Catalyst end of life activity [Ke]
v. Catalyst pressure drop
vi. SO_2 oxidation
1. Activity test conditions [AV, Temperature, NH_3:NO_X MR]

Table 3 Catalyst Product Specification Data for Catalyst Layer Additions

Because the utility will be responsible for managing the integration of the layer addition and determining the expected performance, most utilities will prefer to build some experience with SCR and develop a solid understanding of catalyst characteristics and requirements before utilizing the catalyst product specification approach. If the catalyst product specification approach is selected, the catalyst supplier should typically provide the information described in Table 4 for evaluation by the owner.

Catalyst Supplier Guarantees and Supporting Data
a. Initial catalyst activity [Ko, $Nm^3/(h\text{-}m^2)$]
b. End-of-life catalyst activity [Ke, $Nm^3/(h\text{-}m^2)$]
c. Catalyst activity test conditions
i. Temperature [°C]
ii. Area velocity [AV, $Nm^3/(h\text{-}m^2)$] (typically = field AV)
iii. NO_X
iv. SO_2
v. SO_3

	vi.	H_2O
	vii.	O_2
	viii	Molar ratio [MR, NH_3:NO_X] (typically = 1)
d.	Catalyst SO_2 conversion [%]	
e.	Catalyst SO_2 conversion test conditions	
	i.	Temperature [°C]
	ii.	Area velocity [AV, $Nm^3/(h\text{-}m^2)$] (typically = field AV)
	iii.	NO_X
	iv.	SO_2
	v.	SO_3
	vi.	H_2O
	vii.	O_2
	viii	Molar ratio [MR, NH_3:NO_X] (typically = 0, without NH_3 injection)
f.	Pressure drop guarantee [Pa per layer]	

Table 4 Catalyst Supplier Guarantees and Supporting Data for Product-Based Catalyst Layer Additions

Conclusions

SCR technology is relatively new in Poland while it continues to be commoditized in other EU countries that have had years of experience with SCR. The utilities in Poland are obliged to the regulatory bodies of the European Union to install air pollution control devices to be in compliance with the LCP directive. This will impose technical demands on the industry, demands that have been conquered in the past. Europe and the United States have a broad spectrum of experience and a wealth of knowledge in the designing of SCR catalyst, SCR systems and the management of these air pollution control devices.

Utilities and catalyst suppliers will need to work together closely to clearly define the performance requirements, specifications, and commercial guarantees associated with initial charges of SCR catalyst as well as the subsequent management of future layers.