

**FIRST APPLICATION OF BABCOCK-HITACHI K.K.
LOW SO₂ TO SO₃ OXIDATION CATALYST
AT THE IPL PETERSBURG GENERATION STATION**

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ABSTRACT

This paper characterizes three new low-oxidation catalysts currently being offered by Babcock-Hitachi. They allow for significantly reduced SO₂ oxidation for new Selective Catalytic Reduction (SCR) systems and can minimize additional SO₂ oxidation when older SCR systems require catalyst additions. These new innovations are allowing generators to lower their cold-end corrosion, minimize the formation of ammonium salts while also significantly reducing the propensity for blue plume and acid mist emissions.

This paper discusses the new catalysts and their properties with regard to DeNO_x catalyst activity and SO₂ oxidation rate. It includes a general discussion of the impact upon new SCR units and the effect they can have on catalyst management programs.

In addition, it discusses the design of two SCR systems recently installed at the Indianapolis Power & Light Company (IPL) Petersburg Generating Station located in Petersburg, Indiana. Performance test results are presented substantiating the overall design and the performance of the low-oxidation catalyst.

INTRODUCTION

Throughout the industry, the oxidation of sulfur dioxide (SO_2) is taking a more prominent role in decisions impacting Selective Catalytic Reduction (SCR) systems and other equipment downstream from the boiler. The oxidation of SO_2 to SO_3 detrimentally impacts plant operation as well as the surrounding environment. IPL was well aware of the SCR catalyst SO_2 to SO_3 oxidation issues and worked with Foster Wheeler to design an SCR system that would minimize these impacts. This paper introduces and discusses new SCR catalysts recently made available by BHK with extremely low SO_2 oxidation rates.

The increase of SO_3 from the flue gas passing over the SCR catalyst increases the sulfuric acid content of the flue gas. This increased H_2SO_4 exacerbates corrosion by raising the cold-end condensation temperature, thereby allowing more acid to condense on the cold side of the air preheaters and other downstream equipment. Furthermore, H_2SO_4 acid mist can add to the opacity of the flue gas leaving the stack and may cause a particulate air permit violation. Finally, and perhaps the most egregious impact of this increased acid, is the effect it can have on surrounding areas. It was first noted in Germany after the installation of a SCR system. The acid mist leaving the stack reached the ground level and ruined the paint of cars in the plant parking lot. The solution to the problem was a parking lot roof.

Higher SO_3 in the flue gas also increases the formation of ammonium bisulfate (ABS) in downstream equipment. ABS (NH_4HSO_4) is formed from the SCR NH_3 slip, SO_3 and water vapor. It is sticky and adheres to the downstream surfaces, in particular those within the air preheater. This increases the probability of air preheater pluggage, which causes increased frequency of washing, which typically requires a boiler outage.

There are a number of solutions to air preheater ABS problems. Open flow channels in the air preheater can be replaced with closed channels, increasing the cleaning efficacy of sootblowing. Cold-end steel surfaces can be replaced with enameled surfaces to decrease the adherence potential of the ABS. The cold-end baskets can be increased in depth and often the usual three layers of baskets (cold, intermediate and hot) are reduced to two (cold and hot). Since layer-to-layer intersections can be nucleation sites for ABS formation, eliminating one layer reduces the number of intersections from two to one. It also allows for placement of the single cold-hot intersection into a region where the temperature is not conducive to ABS formation. The final and most effective solution to reducing ABS pluggage is simply to reduce the SO_3 by judicious choice of SCR catalyst. Although the NH_3 concentration will usually govern how much ABS can form, lower SO_3 concentrations will reduce the likelihood of ABS formation.

In addition to the above problems, increased SO_3 can also combine with the SCR ammonia slip and water vapor to form ammonium sulfate. Ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$) is similar to the formation of ABS and is governed by the flue gas conditions. The $(\text{NH}_4)_2\text{SO}_4$ is a particulate and will increase the particulate matter

(PM) leaving the stack. As PM is a permit-restricted pollutant, increased PM emissions are highly undesirable.

Finally, many existing SCR systems have been designed with space for spare catalyst. Adding this spare layer at the end of life of the initial catalyst charge increases the SO₂ oxidation potential from 33 to 50%, depending upon whether the initial charge was filled with 3 or 2 layers, respectively. Some reactors have been designed with two (2) spare layers and an initial charge that occupies two (2) layers. In this case, when all spare layers are filled the SO₂ oxidation rate would double. Having a low SO₂ to SO₃ oxidation catalyst to fill these spare layers may be considered essential to minimize downstream equipment impacts.

Although there are methods to overcome the impact of additional SO₃, including additives to combine it into less troublesome forms, the most efficient solution is to minimize its production. Thus there has been a need for a new class of highly active SCR catalysts that have lower SO₂ oxidation rates. BHK has developed a new class of commercially available catalysts and are currently operating on two (2) utility sized SCR systems firing eastern bituminous coal. This paper presents this new class of catalysts, and the first application describing the design, operation and test results of the SCR systems.

NEW CX TYPE SCR CATALYSTS

Three (3) new catalyst formulations are being offered. Compared to the most active SCR catalysts for coal-fired duty on the market, these new formulations offer some activity advantages along with reduced SO₂ oxidation.

The most active of these new catalysts, "CXM", is more active than traditional catalysts over the entire range of SCR temperature operation, but the unit SO₂ oxidation rate is very comparable. Thus with more activity, a smaller volume (10-20%) can be achieved and subsequently the total SO₂ oxidation rate is reduced about 10-20%. A lower volume of catalyst can result in lower pressure drop and reduced SO₂ oxidation.

The mid-range activity offering is the "CX" Catalyst. This catalyst has higher activity (above about 650°F) than traditional catalysts, while having about half the SO₂ oxidation rate. Below 650°F, this catalyst is only slightly lower in activity than its predecessors. Thus for boilers that operate over the entire load range but need added SO₂ oxidation reduction, this provides distinct advantages. The CX catalyst tends to require more volume than the CXM, but its activity and oxidation characteristics may justify the additional catalyst.

The lowest SO₂ oxidation catalyst is the CXL. This catalyst has higher activity than traditional catalysts above about 725°F. At lower SCR operating temperatures, the activity may drop to 10-15% below those currently in use. The SO₂ oxidation rate is about a third of the usual catalysts. This catalyst can be very effective in reducing SO₂ oxidation for base-loaded boilers or those that operate with higher exit gas temperatures.

For most typical operating conditions, these new catalysts have volumes 10-20% below traditional catalysts. The SO₂ oxidation rates, however, are substantially lower. Table 1 gives a relative comparison of these catalysts, including the more traditional “C3” catalyst.

Catalyst Type	SO ₂ to SO ₃ Oxidation Rate (%) NO ADDITIVES REQUIRED		
	< 0.5	< 1.0	< 1.5
Standard C3	-	< 700 °F	< 740 °F
CXM	< 650 °F	< 720 °F	< 745 °F
CX	< 720 °F	< 780 °F	< 815 °F
CXL	< 780 °F	< 840 °F	-

Design Conditions:
 Inlet NO_x concentration: 300 ppm
 DeNO_x Efficiency: 90 %
 Slip NH₃: < 2 ppm
 Lifetime: 24,000 h

Table 1: Applicable Temperature Ranges for New Installations

For the design conditions noted in Table 1, the relative merits of each new catalyst become evident. The new catalyst volumes do not vary much from that of traditional catalyst, and in some instances the volumes are less. Note the traditional catalyst cannot achieve SO₂ oxidation of 0.5% for the given conditions. The upper operating temperature limit for the CXL catalyst is 840 °F.

For existing SCRs, the new catalysts offer lower than originally anticipated SO₂ oxidation rates with the addition of catalyst into the spare layers, or the replacement of old layers. For current SCR systems experiencing problems brought about by excessive SO₃ production, the new catalysts offer a straightforward remedy for reduced formation of SO₃ that will either eliminate or reduce the need for chemical injection options that increase both operating and maintenance costs. As for new SCR systems in either new boiler or retrofit applications, these new catalysts provide an initial approach to minimize SO₃ and all its inherent difficulties. This advantage will likely result in low SO₂ oxidation becoming the benchmark for new SCR applications utilizing medium to high-sulfur bituminous fuels.

PETERSBURG

The first application in the U.S. for these new catalysts is the CXL type, which is currently operating in the IPL Petersburg SCR units. Foster Wheeler was selected by IPL to retrofit Petersburg Units 2 and 3, with SCR systems. A major technical concern was the formation of SO₃ within the SCR system. Foster Wheeler’s review of the catalyst options resulted in the selection of the BHK “CXL” catalyst. This catalyst exhibited the high activity (90% DeNO_x) and provided the low SO₂ oxidation that Foster Wheeler and IPL project required.

Description

The Petersburg station is located in Pike County, Indiana. Unit 2 is a pulverized coal, tangentially-fired, drum type, balanced draft boiler which was placed in service in 1969, and is rated at 463 MWe (MCR). It fires locally mined eastern bituminous coal and has fuel oil igniters for light off. The steam generator is equipped with two (2) Ljungstrom regenerative air preheaters and has an electrostatic precipitator (ESP) followed by a wet Flue Gas Desulphurization (FGD) system. The Unit 2 SCR arrangement is shown in Figure 2.

Unit 3 is also a pulverized coal, tangentially fired, drum type, balanced draft boiler which was placed in service in 1977, and is rated at 563 MWe (MCR). It fires locally mined eastern bituminous coal and has fuel oil igniters for light-off. The steam generator is equipped with two (2) Ljungstrom regenerative air preheaters and has an electrostatic precipitator (ESP) followed by a wet Flue Gas Desulphurization (FGD) system. The Unit 3 SCR arrangement is shown in Figure 3.

Fuel

There are several local eastern bituminous coals fired in both boilers. These may be summarized as shown in Tables 2.

Parameter	Typical (%)
Moisture	--
Ash	9.0
Carbon	73.6
Hydrogen	5.0
Oxygen	7.6
Nitrogen	1.3
Sulfur	3.5

Table 2a: Ultimate Analysis (Dry)

Parameter	Range (% By Weight)
SiO ₂	34.89 – 56.0
Al ₂ O ₃	16.13 – 26.21
TiO ₂	0.68 – 0.95
FeO ₂	10.92 – 15.60
CaO	See Table 2c
MgO	0.26 – 1.35
Na ₂ O	0.22 – 1.27
K ₂ O	0.75 – 3.24
SO ₃	0.2 – 5.25
P ₂ O ₅	0.02 – 0.78

Table 2b: Ash Mineral Analysis – Ignited Basis

Coal	As, ppm	CaO, %	% Fired
A	14.40	2.07	19.3
B	11.07	1.47	14.8
C	8.10	2.16	9.0
D	8.05	2.48	47.2
E	5.74	2.40	9.7

Table 2c: Average Arsenic and Calcium Concentrations on Dry Basis

The fuels differ but estimates were given as to the annual firing percentages of each coal as listed in Table 2c.

SCR System Requirements

SCR Catalyst Design Requirements

Petersburg Units 2 and 3 were slated for a seasonal NOx reduction, May through September operation, but were designed for year round operation. The operating conditions that Foster Wheeler used as the basis of the SCR catalyst design are given in Table 3.

Parameter	Units	Unit 2 SCR Inlet Conditions	Unit 3 SCR Inlet Conditions
Fuel	-	Coal	Coal
# of Reactors	Number/Boiler	2	2
Flue Gas Flow	Lb/hr	4,485,000	5,429,000
	Nm ³ /hr	1,552,065	1,878,943
Flue Gas Temp.	°F	778.1	741.6
	°C	414.5	394.1
Flue Gas Inlet			
O ₂	% Volume Dry	4.59	4.65
H ₂ O	% Volume	8.78	8.96
SO ₂	ppmvd @ 3% O ₂	2,645	2,225
SO ₃	ppmvd @ 3% O ₂	25	21
Dust	mg/Nm ³	9,800	10,200
NOx	ppmvd @ 3% O ₂	303.1	335.6
Inlet Variations			
Temperature	± °F	20	20
NH ₃ /NOx	% RMS	5	5
Gas Distribution	% RMS	15	15

Table 3: SCR Catalyst Inlet Conditions

Guaranteed Item	Units	Unit 2 SCR Outlet Conditions	Unit 3 SCR Outlet Conditions
DeNOx Efficiency	%	≥ 90	≥ 90
NH ₃ Slip – mean	ppmvd @ 3% O ₂	2	2
Catalyst ΔP Initial Charge	In. W.G.	≤ 1.4	≤ 1.8
Catalyst Life	Hours	24,000	24,000
SO ₂ Oxidation	%	≤ 0.5	≤ 0.5

Table 4: BHK's Guaranteed Catalyst Design Requirements

The guaranteed SCR catalyst performance requirements are shown in Table 4. From design temperatures and overall NOx reduction requirements shown in Table 1, CLX catalyst design was utilized for both Units 2 and 3. Each SCR system was equipped with an initial charge of two (2) catalyst layers with one (1) spare layer for future catalyst addition.

A critical aspect of designing the catalyst charge for a specific application is establishing the allowable variations for inlet temperature, NH₃/NOx and flue gas velocity distributions. Foster Wheeler established that the inlet conditions for the catalyst based upon past experience with BHK and the overall SCR system layout. These conditions helped to establish the final catalyst volume.



Figure 1: Petersburg Station

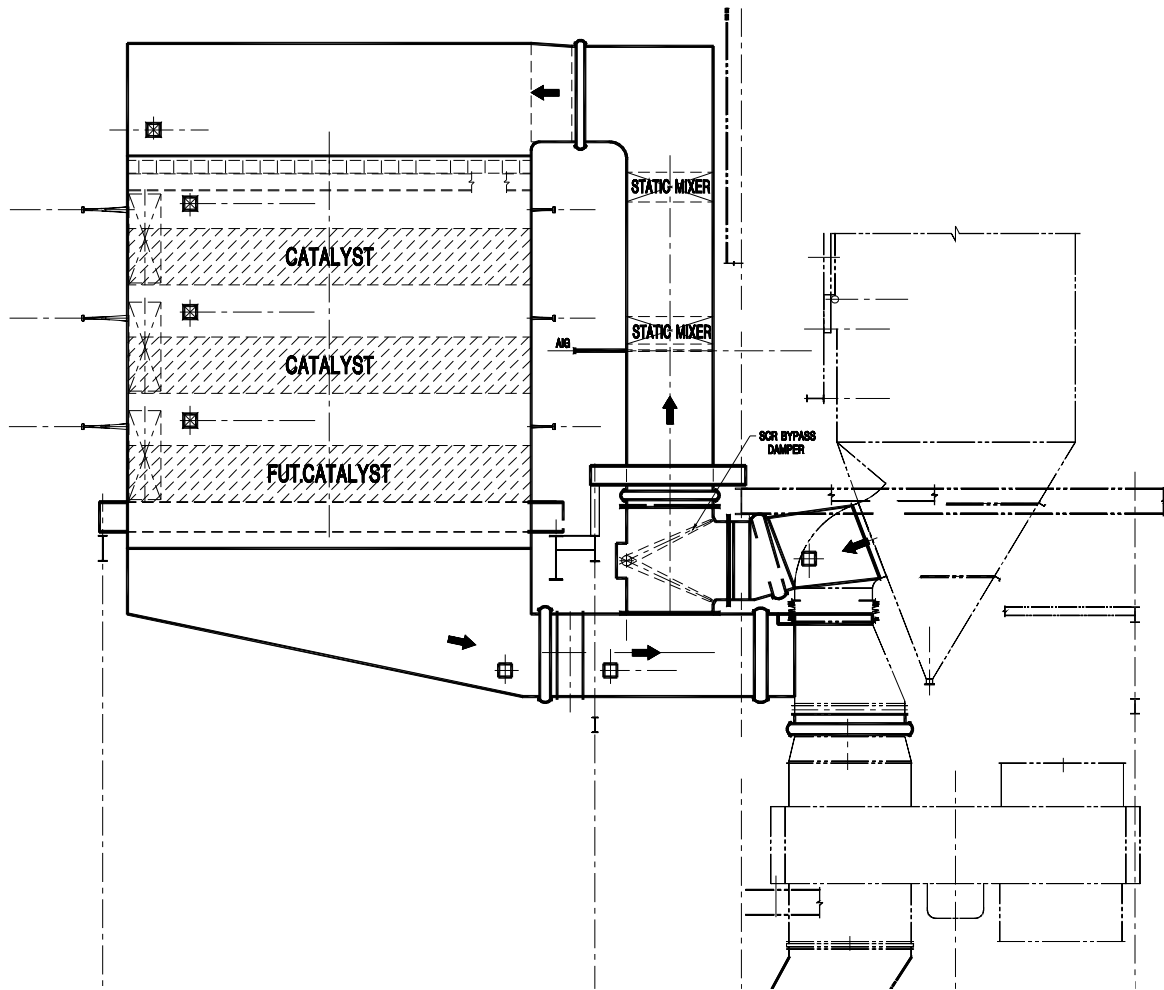


Figure 2– Unit 2 SCR System Arrangement

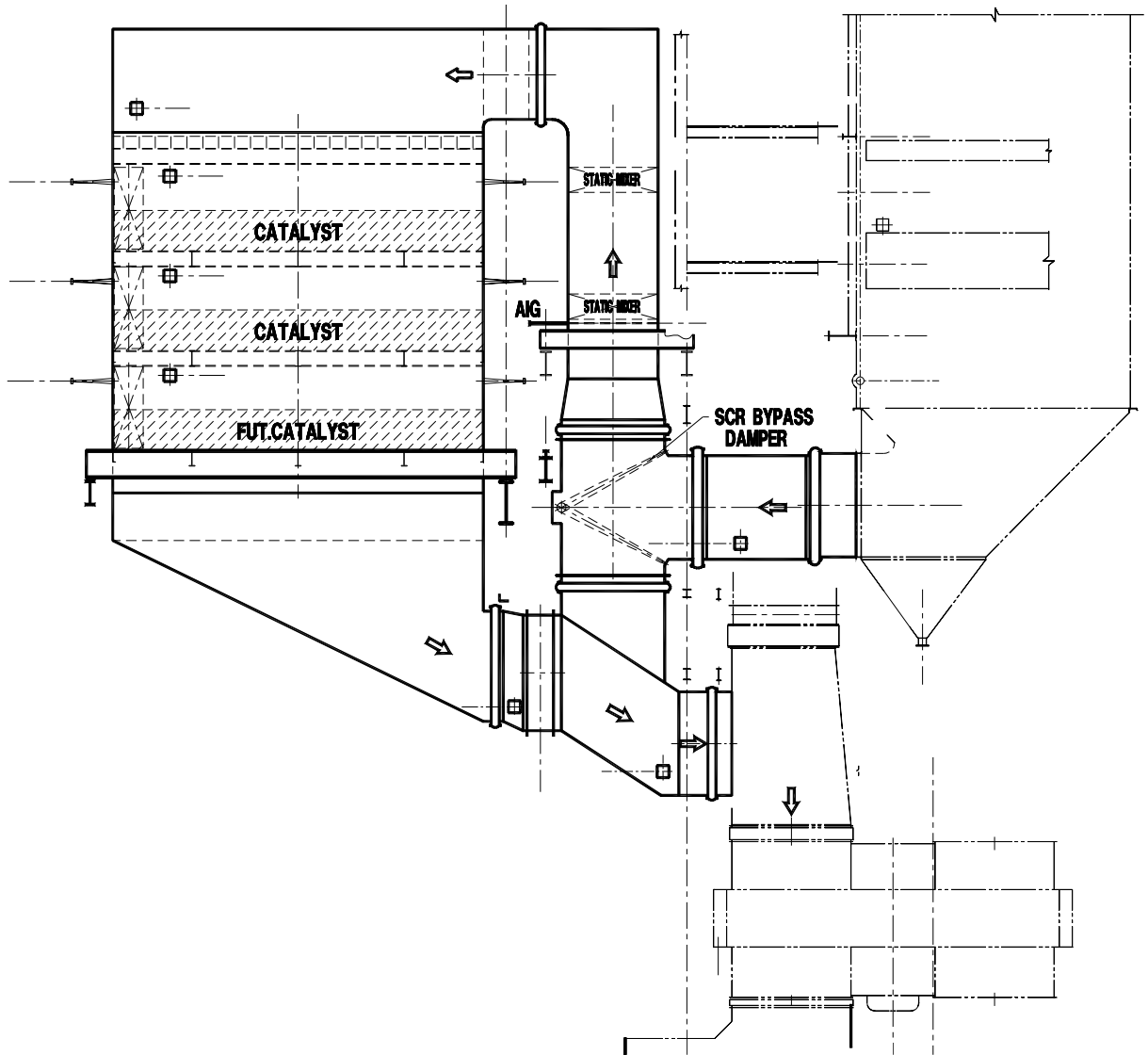


Figure 3 – Unit 3 SCR System Arrangement

SCR System Retrofit Design

The key to a successful SCR system is well-distributed ammonia, gas, particulate and temperature at the reactor inlet. For each of the Petersburg SCR systems, Foster Wheeler utilized a 1/12th scale flow model to determine the optimum arrangement of flow control devices needed to meet the flow, temperature and ammonia distribution requirements within the SCR. The flow model extended from the exit of the economizer to the air preheaters (see Figures 4 and 5). The model included simulations of the SCR inlet/outlet flues, SCR bypass flues, AIG, static mixers (see Figure 6), catalyst layers, and air preheaters.

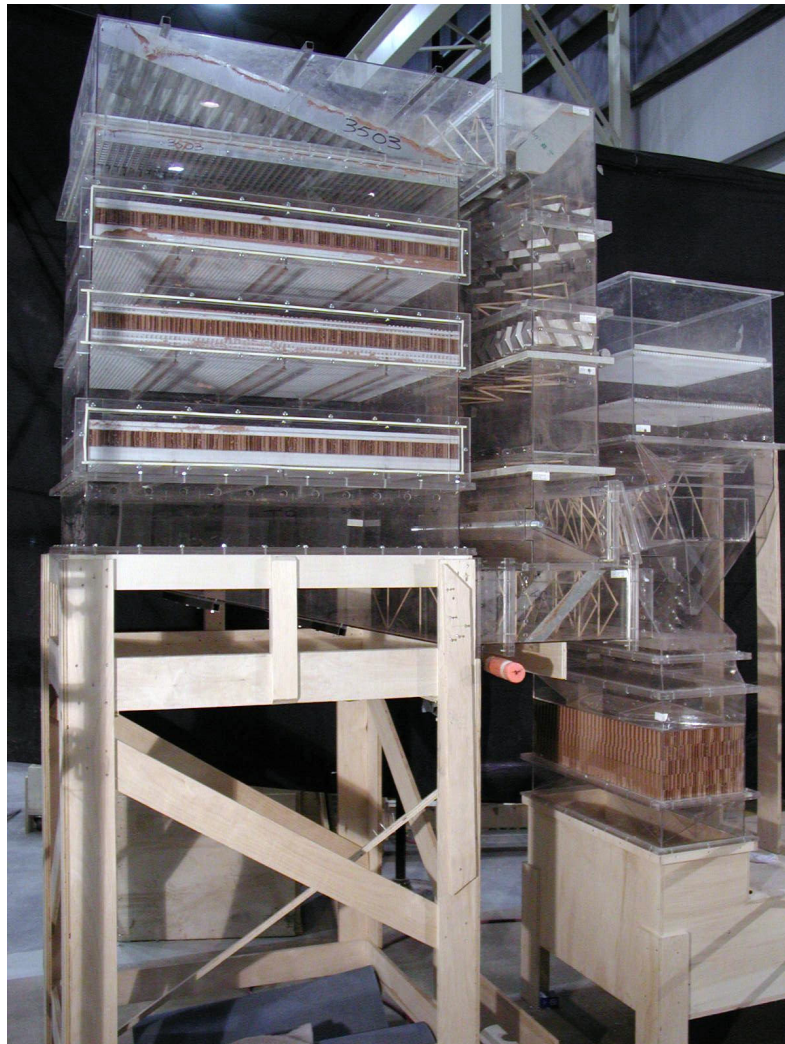


Figure 4 – 1/12th Scale Flow Model (Unit 2)



Figure 5 - 1/12th Scale Flow Model (Unit 3)



Figure 6 – Scale Model of ALG and Static Mixers (Unit 3)

As required in Table 3, the primary objective of the modeling performed by Foster Wheeler is to meet flow and ammonia distributions at the catalyst inlet. Since these units were not equipped with economizer bypass systems, it was not deemed necessary to simulate temperature in the model.

The following procedures were used to simulate and optimize these objectives:

Flow Distribution - Ambient air flow, was measured in the model at the point of interest. Standard pitot-static tubes were used to measure velocity distribution in the transport flues, and a hot-wire anemometer was used to measure the velocity field and flow angles at the catalyst inlet and outlet.

Ammonia Distribution - A tracer gas (CO) was uniformly injected into the AIG pipes, and the CO concentration field was measured at the catalyst inlet. The distribution of the tracer gas was used to infer ammonia distribution.

Pressure Drop - Model pressures were measured and then corrected to full-scale flow and temperature conditions.

Ash Dropout - Model cork-dust particles were injected into the model, taking into account the differences between the actual fly-ash, model scale and temperature/flow conditions. The results gave general indications of where ash dropout could occur in the full-scale system.

Results

Flow Distribution

As discussed previously, static mixers were employed to aid in distributing ammonia and the flue gas at the catalyst. Turning vanes were installed in the inlet flues to provide uniform flow distribution at the AIG and catalyst. The turning vane designs, in conjunction with the static mixers, were then optimized to produce acceptable flow distribution into the catalyst. A flow distribution of <12 percent RMS was achieved at the catalyst inlets for both Units 2 and 3. This exceeded (met) BHK's requirement of ≤15 percent RMS.

Ammonia Distribution

The integral AIG and static mixer system was found to be very beneficial in providing both uniform gas and ammonia distribution into the catalyst. Final ammonia distribution at the catalyst inlet was measured at 4 percent RMS. One of the advantages of this mixing system is the degree of homogenization of the NO_x and ammonia, without the need for AIG tuning. The thorough mixing takes place throughout the load range, with changing gas, temperature and boiler exit NO_x distributions.

System Pressure Drop

Overall system pressure drop was measured and reported throughout the modeling process. Predicted and modeled pressure drop measurements agreed very well, to ensure a limited increase in losses due to flow control and mixing device modifications. System pressure drop measurements in the full-scale system have indicated very good agreement between both predicted and modeled values.

Ash Dropout

Ash dropout testing was performed after flow-distribution optimizations were completed. Overall, little ash dropout was observed in the model.

Initial results on key system performance criteria indicate that the recommendations generated from the modeling results have proven very effective. Overall the model study proved to be a critical step in project execution.

Petersburg Performance Test Results

Performance testing was used to establish that the Unit 2 and 3 SCR systems met their respective requirements. The tests were performed on both units in June 2004.

Traverses consisting of a 6 x 4 array at the exit of the second catalyst layers were used to record NO_x. Initially, no ammonia is injected into the SCR to allow for the measurement of inlet NO_x. Ammonia was then injected and outlet NO_x measurements were obtained. Measurements with four (4) point traverses in a narrow flue sections upstream of each of the two (2) air preheater inlets were used to determine the NH₃ slip from each reactor.

Traverses upstream of each of the ammonia injection grids were used to measure the SO₂ and SO₃ inlet values. Measurements prior to ammonia injection eliminate the possibility of NH₃ interference. SCR outlet SO₂ and SO₃ were measured in the flues downstream of the reactors.

Manometers were utilized to measure the pressure drop across the SCR system and also across just the catalyst.

All measurements were recorded along with the actual SCR operating conditions. BHK's catalyst performance correction curves were used to correct the actual measured results for [to] design conditions. The performance test results, after correcting to design conditions, are shown in Table 5.

Parameter	Units	Guarantees	Performance Test Results	
			Unit 2	Unit 3
DeNO _x Efficiency	%	90	90	90
NH ₃ Slip	ppmvd @ 3% O ₂	≤ 2	0.6	1.2
Catalyst ΔP	In. W. G.	≤ 1.4 (Unit 2) ≤ 1.8 (Unit 3)	1.1	1.5
SO ₂ Oxidation	%	≤ 0.5	≤ 0.3	≤ 0.3

Table 5: Performance Test Results

CONCLUSIONS

The first U. S. application of the new Babcock-Hitachi low SO₂ oxidation SCR catalysts has been very successful. Actual measured results were better than predicted. These new catalysts usher in new prospects to reduce sulfuric acid cold end corrosion and acid mist opacity while keeping ground level acidity to a minimum. They reduce the propensity for increased particulate matter and reduce the potential for air preheater plugging when ammonia is present.

For existing SCRs, these new catalysts offer lower than originally anticipated SO₂ oxidation rates with the addition of catalyst into the spare layers or the replacement of old layers. For current SCR systems experiencing problems brought about by excessive SO₃ production, they offer a straightforward remedy and avoidance of chemical injection to alleviate the problem. For new SCR systems, these new catalysts offer an initial approach to minimize SO₃ production with all its inherent difficulties. As with all Foster Wheeler SCR systems, gas flow modeling is a critical step in assuring optimized catalyst operation and long-term performance.