Application and Operating Results of Low SO_2 to SO_3 Conversion Rate Catalyst for DeNOx Application at AEP Gavin Unit 1

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Abstract

The impact of increased SO2 to SO3 oxidation due to the installation of an SCR on many units in the United States that burn high sulfur coal was more significant than expected. Soon after the SCR start up on Gavin Units 1 and 2, AEP recognized this issue and began the evaluation of several mitigation techniques and technologies to reduce SO_3 emissions. At the same time, the development of low SO_2 to SO_3 conversion rate catalyst became one of the most important research projects for catalyst manufacturers. After extensive research work, Babcock-Hitachi developed low SO_2 to SO_3 conversion rate catalyst while maintaining high DeNOx activity. This paper presents (1) the development efforts of this new SO_2 to SO_3 conversion rate catalyst, (2) the results of the AEP SO_3 mitigation study, and (3) the performance test results of Gavin Unit 1 SCR after the replacement of the existing catalyst with Hitachi low SO_2 to SO_3 conversion rate catalyst.

Identification of the Necessity for Low SO_2 to SO_3 Conversion Rate Catalyst

The first catalytic DeNOx system for large utility boilers was commissioned for operation in 1977 in Japan. Since then, SCR applications have been applied for various fuels such as gas, oil and coal, and the installations have expanded to many industrialized countries around the world.

In the past several years, the SCR units in the US that burn high sulfur (3-7%) Eastern Bituminous coal experienced operational difficulties such as severe blue plume generation and acid mist emission. The increased SO3 concentration also causes (1) acceleration of corrosion of downstream equipments, (2) increased possibility of ammonium bisulfate (ABS) formation within air preheater elements and (3) increased PM emission.

To overcome this problem, several research efforts to reduce SO_3 emissions were conducted such as injecting different additives to combine SO_3 into less troublesome forms.

The development of low SO_2 to SO_3 conversion rate catalyst can be the most effective solution to minimize the production of SO_3, and therefore it became a targeted research project for catalyst manufacturers.

The SO_2 to SO_3 conversion rate is closely related with DeNOx activity so that when the SO_2 to SO_3 conversion activity was reduced, larger catalyst volume was required to maintain the required DeNOx performance. Therefore, the development had to focus on improving DeNOx activity while lowering SO_2 to SO_3 conversion activity. Through diligent research work, changes in the catalyst manufacturing process and the screening of new materials by Babcock-Hitachi (BHK) resulted in the development of low SO_2 to SO_3 conversion rate catalyst while maintaining high DeNOx activity. Since this break through several years ago, this new catalyst has been successfully applied at several commercial applications
(see Table 7).

Development of Low SO_2 to SO_3 Conversion Rate Catalyst

The development of low SO_2 to SO_3 conversion catalyst focused on the SCR units in the US firing high sulfur Eastern Bituminous coals with high DeNOx efficiency, low ammonia slip and a gas temperature range from 690^0 F to 790^0 F. It was decided that the target SO_2 to SO_3 conversion rate of less than 0.5% for initial installation would be optimal.

A detailed discussion of this development was addressed in a paper at the ICAC Clean Air Technologies and Strategies in March, 2005 titled," Development and Operating Results of Low SO_2 to SO_3 Conversion Rate Catalyst for DeNOx Application", (see reference section). The results of this research were the development of a new series of low SO_2 to SO_3 conversion rate catalysts called the CX series. The performance results for these catalyst types, for various temperatures, are shown in Table 1.

Table 1 Applicable Temperature Ranges for New Catalyst

Catalyst Type	SO_2 to SO_3 Conversion Rate* (%)		
	0.5	1.0	1.5
Base	-	< 700 °F	< 730 °F
CXM	< 645 °F	< 715 °F	< 740 °F
CX	< 715 °F	< 780 °F	< 815 °F
CXL	< 780 °F	< 830 °F	-

* SO_2 to SO_3 Conversion Rate for initial installation.

SCR Start Up and Initial Observation of Increased Levels of SO3 at Gavin Unit 1

The Gavin Plant is located in Cheshire, Ohio. It has two 1300 MWnet sister Units. Each Unit has B&W pulverized coal, dry bottom boiler. The Gavin Plant has been burning high sulfur (6.5 lb SO_2/mmBtu) coal since mid 1980's.

The initial start up of the SCR at Gavin Unit 1 was on May 1, 2001. This is the largest SCR installed on a US boiler. The Gavin Units has always burned a high sulfur coal and when the initial catalyst design parameters were specified, the SO2 to SO3 conversion rate was 1.5% which was the industry standard. The SCR experiences in Japan and Europe did not have a need for lower oxidation rates since the majority of the fuels burned there have lower sulfur.

The SCR arrangement for each Gavin unit was divided into three equally sized parallel reactors to match the three air preheaters. The reactors are a 3 + 1 (three initial layers and one spare) layer design and the catalyst volume for the initial three layers was 2124 m3. The initial design parameters are shown in Table 2.

Table 2 Initial SCR Design Conditions for Gavin Unit 1

Items	Condition
Inlet NOx concentration	500 ppm
SO_2 concentration	3134 ppm
DeNOx efficiency	90 %
Slip NH3 concentration	2 ppm
Life time	16,000 hours
SO_2 Conversion Rate	1.6 %

After the SCR start up, it was obvious that the initial catalyst design parameters resulted in an unacceptable level of SO_3 exiting the stack and some type of modification and/or mitigation was required. A detailed study followed to determine the best solution to resolve this issue for the life cycle of the unit. A summary of this study is discussed below.

Results of the AEP Study to Mitigate SO_3 at Gavin Units 1 and 2

Following the start up of the SCR at Gavin unit 1 in 2001, AEP recognized the need to lower the SO_3 emission and began a study to determine the best means to mitigate the increase of SO_3 over the life cycle of the plant. The initial operation of the SCR was during the Ozone Season of May 1st through September 30th. However year round operation was scheduled for as early as 2009.

Some of the mitigation techniques evaluated by AEP are listed in Table 3.

Table 3 SO_3 Mitigation Techniques

- WESP
- Magnesium Hydroxide Slurry Injection in boiler
- Low-Conversion SCR Catalyst
- Hydrated Lime Injection at air preheater outlet
- Trona Injection at air preheater outlet
- Ammonia Injection at air preheater outlet

- Reagent Combinations
    - Magnesium Hydroxide in boiler and Ammonia at air preheater outlet
    - Magnesium Hydroxide in boiler and Lime at air preheater outlet
    - Magnesium Hydroxide in boiler and Trona at air preheater outlet

The AEP evaluation determined that the best life cycle cost for this unit was to replace all three layers of existing catalyst prior to the end of life and to use Trona injection at air preheater outlet.

Operational Results of Low SO_2 to SO_3 Conversion Rate Catalyst at Gavin Unit 1

(1) Gavin Unit 1 was not the first application of low SO_2 to SO_3 conversion rate catalyst. Unit 2 and 3 at AES Petersburg were the first SCR installations of the Babcock-Hitachi (BHK) low SO2 to SO3 conversion rate catalyst and was successfully tested in 2004. Gavin was unique in that the existing catalyst was being replaced to minimize the amount of SO3 mitigation sorbent consumption.

Fig. 1 AEP Gavin Station

Gavin station utilizes several local high sulfur eastern bituminous coals. Analysis of these coals are summarized in Table 4. Table 5 shows the design basis of DeNOx catalyst for Gavin unit 1.

As shown in Table 5, the application also required DeNOx efficiency of 90% with ammonia slip less than 2 ppm. These conditions require the DeNOx plant to be designed to achieve very good distributions for NH_3/NOx, temperature and gas velocity. The DeNOx system supplier had initially conducted physical flow model testing to achieve the following inlet variations.

NH_3/NOx	Less than ±5 % RMS
Temperature	Less than ±20 °F
Gas velocity	Less than ±15 % RMS

Table 4 Coal Analysis Data for Gavin

Ultimate Analysis (Dry)	
Items	Typical (%)
Moisture	7.65
Ash	9.3
Carbon	66.95
Hydrogen	4.71
Oxygen	6.34
Nitrogen	1.25
Sulfur	3.75

Ash Mineral Analysis	
Items	Range (%; as ash)
SiO_2	45.7
Al_2O_3	20.65
TiO_2	0.9
Fe_2O_3	23.3
CaO	3.5
MgO	0.85
Na_2O	0.5
K_2O	1.65
SO_3	2.5
P_2O_5	0.45
As in coal (ppm)	21

Table 5 Design Basis of Low SO_2 to SO_3 Conversion Catalyst for Gavin

Items	Unit	Gavin #1
No of Reactor	Number/Boiler	3
Generation Capacity	MW	1300
Flue Gas Flow	m^3/h(Normal)	1,497,850
Flue Gas Temp.	°C	371.1
Inlet O_2	%, Dry	3.5
H_2O	% (Volume)	8.2
SO_2	ppmvd @ 3% O_2	3130
SO_3	ppmvd @ 3% O_2	31
NOx	ppmvd @ 3% O_2	500
Dust	mg/m^3(Normal)	12,360
DeNOx Efficiency	%	90
Slip NH_3	ppmvd @ 3% O_2	Less than 2
SO_2 to SO_3 conv.	%	0.38
Catalyst Life	hours	16,000

For the DeNOx plants at Gavin, sonic horns were applied to the first reactor and conventional soot blowers were installed on the other two reactors.

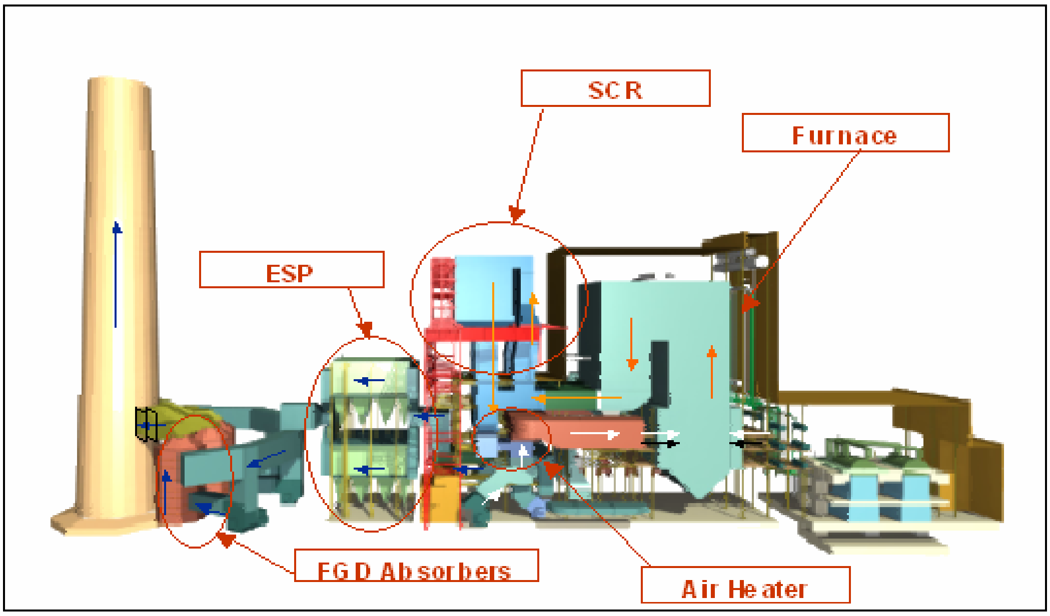

Fig. 2 Arrangement of DeNOx Plant for Gavin Unit 1

(2) Operating results of SCR at Gavin Unit 1

Following the removal of the old catalyst and the installation of the new Hitachi catalyst in the spring of 2005, the SCR went into operation. After the initial adjustments, performance tests were performed in June 2005.

The performance test results are summarized in Table 6.

Table 6 Performance Test Results

Parameters	Units	Guarantee	Test Results
DeNOx Efficiency	%	90	94
NH_3 Slip	ppmvd @ 3% O2	Less than 2	0.4
Catalyst ΔP	inch W.G.	Less than 3	Not tested
SO_2 to SO_3 Conversion Rate	%	0.38	< 0.1

As shown in Table 6, the catalyst installed in DeNOx plants at Gavin Unit 1 met all of the guarantees. In particular, the measured SO_2 to SO_3 conversion rate was considerably lower than the guaranteed 0.38% conversion rate.

Gavin Unit 2 DeNOx plants still had original catalyst in 2005 ozone season. A comparison of Trona injection rates between Unit 1 and Unit 2 indicates that the Trona consumption of Unit 1 which has Hitachi low conversion rate catalyst is approximately 35% of that of Unit 2.

The SCR at Gavin operated successfully during the 2005 Ozone season without any problem for both DeNOx and boiler systems. An inspection of Unit 1 DeNOx plants were conducted after 2005 ozone season. Representative observation results were shown in Fig. 3 and 4. As shown in the Figures, neither abnormal ash accumulation nor erosion of catalyst was observed.

Fig. 3 Inside Inspection Result – General View –

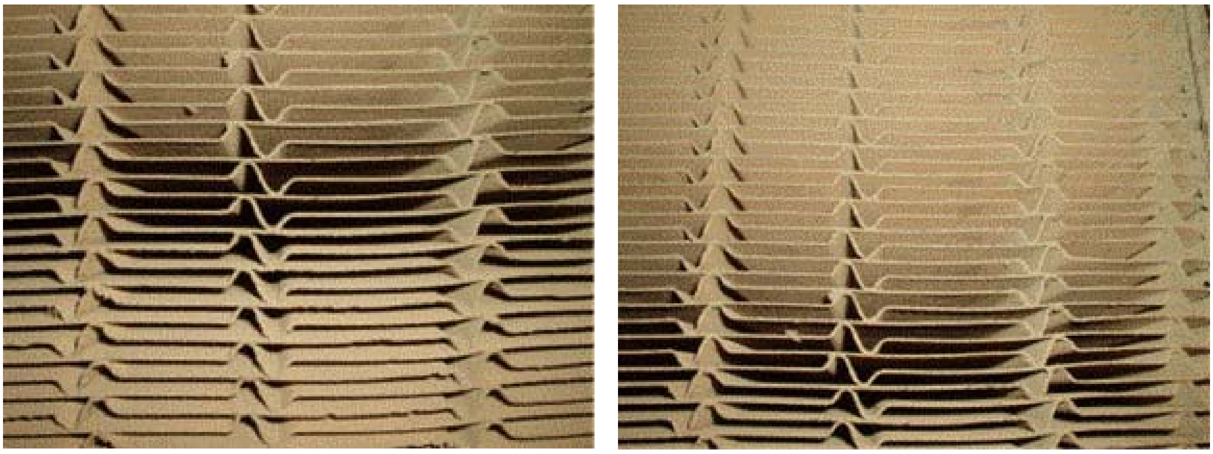

Fig. 4 Inside Inspection Results – Close-up Observation of Catalyst -

(3) Other applications

The newly developed CX Series Type catalyst was supplied to various DeNOx plants. Table 7 shows the experience list of CX Series Type catalyst that was supplied up to the spring of 2005.

Table 7 Experience List of CX Series Type Catalyst

No.	Plant Name	Catalyst Type	Start Operation	Note
1	Petersburg 2	CXL	2004	New Installation
2	Petersburg 3	CXL	2004	New Installation
3	Farge	CXM	2004	Replacement
4	Datteln	CXM	2004	Replacement
5	Muskingum River	CX	2005	New Installation
6	Gavin 1	CXL	2005	Replacement
7	Keystone 1	CXM	2005	Addition
8	Trimble County 1	CXM	2005	Addition
9	Logan	CXM	2005	Replacement
10	Lambton 4	CXL	2005	Addition
11	Duernrohr 1	CXM	2005	Replacement

Conclusion

Babcock-Hitachi developed new CX Series Type catalyst having low SO_2 to SO_3 conversion rate while maintaining high DeNOx potential. Since its first application, it has consistently achieved low SO_2 to SO_3 conversion rates as low as 0.1% even at elevated temperature above 740ºF.

By application of CX Series Type catalyst in DeNOx plants, the catalyst can achieve various benefits for a wide range of plant applications, operating conditions and fuels.

REFERENCES

J. Cooper, W. J. Gretta, A.C. Favale, H.N. Franklin, *First Application of Babcock-Hitachi K.K. Low SO2 to SO3 Oxidation Catalyst at the IPL Petersburg Generation Station*. ICAC Clean Air Technologies and Strategies, Baltimore, MD, March 2005.