Successful Implementation of Cormetech Catalyst in High Sulfur Coal-Fired SCR Demonstration Project

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Abstract

The U.S. Department of Energy (DOE), Electric Power Research Institute (EPRI), Ontario Hydro, and Southern Company Services (SCS) jointly funded a project under the Innovative Clean Coal Technologies (ICCT) Program to demonstrate the capabilities of Selective Catalytic Reduction (SCR) technology on high sulfur U.S. coal. The demonstration site was at Gulf Power Company's Plant Crist Unit No. 5 (75 MW capacity) near Pensacola, Florida. The demonstration was completed in July 1995.

Cormetech was one of a number of catalyst manufacturers that participated in the program. Cormetech supplied catalyst for two (2) small-scale SCR reactors, one high dust and one low dust. The high dust catalyst was in operation for 10,600 hours and the low dust catalyst was in operation for 5,800 hours. Required performances, including NOx removal and SO2 oxidation, were maintained during the demonstration for both reactors. Moreover, the catalysts are projected to have met required performances well beyond the duration of the demonstration.

The report included herein details the primary field test results performed by SCS and catalyst test results performed by Cormetech during the test period for the reactors containing Cormetech catalyst. Specific results and their impact are discussed, including changes in catalyst performance and properties over time.

I. BACKGROUND

The U.S. Department of Energy (DOE), Electric Power Research Institute (EPRI), Ontario Hydro, and Southern Company Services (SCS) jointly funded a project under the Innovative Clean Coal Technologies (ICCT) Program to demonstrate the capabilities of Selective Catalytic Reduction (SCR) technology on high sulfur U.S. coal. The results of the project are summarized in Topical Report Number 9, Clean Coal Technology - Control of Nitrogen Oxide Emissions: Selective Catalytic reduction (SCR) by The U.S. Department of Energy and Southern Company Services, Inc, May 1997.

The demonstration site was at Gulf Power Company's Plant Crist Unit No. 5 (75 MW capacity) near Pensacola, Florida. The demonstration facility includes a total of nine (9) SCR reactors which were run in parallel. Three (3) 2.5 MWe reactors and six (6) 0.2 MWe. All reactors represent high dust applications (upstream of hot-side ESP) except one 0.2 MWe reactor which was configured as a low dust application (downstream of hot-side ESP).

The two year demonstration project began in June 1993 and concluded in July 1995.

Cormetech was one of a number of catalyst manufacturers that participated in the program. Cormetech designs and manufactures honeycomb catalyst of homogeneous composition for SCR based on licensed technology of Mitsubishi Chemical Corporation and Mitsubishi Heavy Industries. Developmental catalyst was not employed on this project. The specific licensed catalyst technology used has been employed world-wide on a total of 400 units including 75 coal-fired boilers.

Cormetech supplied catalyst for two (2) 0.2 MWe SCR reactors, one high dust and one low dust. The 0.2 MWe reactors were approximately one (1) square foot in cross-section and consisted of three (3) and two (2) layers of catalyst respectively. The catalyst for the low dust reactor was installed in April 1994 as a substitute for another catalyst vendor that withdrew from the test. Therefore, the total number of operating hours was somewhat less for the low dust catalyst versus the high dust.

SCS managed the project from permitting to engineering and construction, as well as, all field operation and testing.

Sootblowing was used regularly on all reactors. The 2.5 MWe reactors were equipped with automatic rake type sootblowers, while the remaining reactors were manually air blown.

In addition to field tests on each reactor, catalyst samples were pulled and returned to each respective catalyst manufacturer. Each manufacturer was responsible for testing and reporting on the state of their catalyst to the project funders.

This paper presents specific field and laboratory data for Cormetech's catalyst. The data is compared to requirements showing that the demonstration was successful. Key flue gas and ash data for Plant Crist are provided in the Appendix to define the conditions under which the SCR was operated.

II. DESIGN CONDITIONS

Performance Design Conditions

Temperature, ^{O}F	700
Superficial Velocity, ft/s	18.1
O_2, vol % wet	3
Inlet NOx, ppmv	400
Inlet SOx, ppmv	~ 2000 (~3% S in fuel)
Molar Ratio, NH3/NOx	0.8
NOx Conversion Target, %	80
Maximum Allowable NH3 slip, ppmv	5
Maximum Allowable Pressure Drop, in H_2O	4
Maximum Allowable SO2 Oxidation, %	0.75
Number of Full Size Layers	3 (High dust) 2 (Low dust)
Catalyst Pitch, mm	7.1 (High dust) 3.7 (Low dust)
Catalyst Length, mm	1000 (High dust) 600 (Low dust)
Space Velocity (SV), Hr^{-1} @ $32^{O}F$, 1 atm	2776 (High dust) 7033 (Low dust)

III. PERFORMANCE RESULTS

A. High Dust (10,600 hours in operation)

Field Results

Ammonia slip remained ≤ 1 ppmv for the duration of the demonstration. This was well below the 5 ppmv maximum allowable slip. No change in ammonia slip over time was detectable (Figure 1).

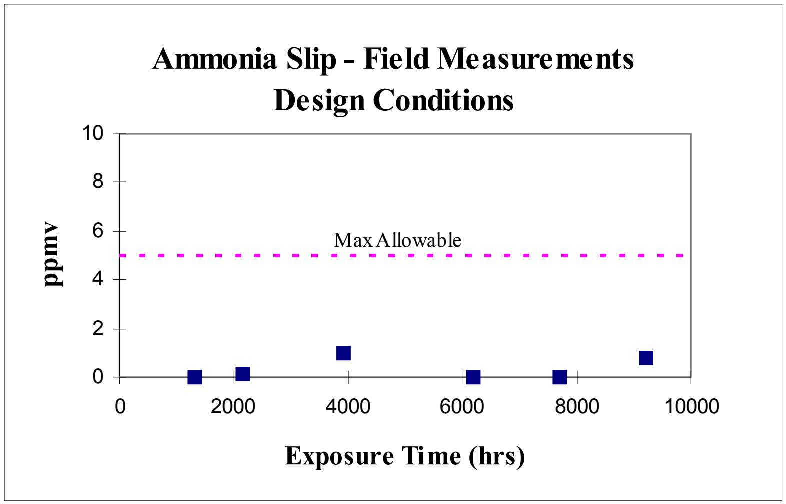

Figure 1

SO_2 oxidation rate remained well below the 0.75% maximum allowable rate for the duration of the demonstration. Average SO_2 oxidation rate was below 0.4%. No change in SO_2 oxidation rate over time was detectable (Figure 2).

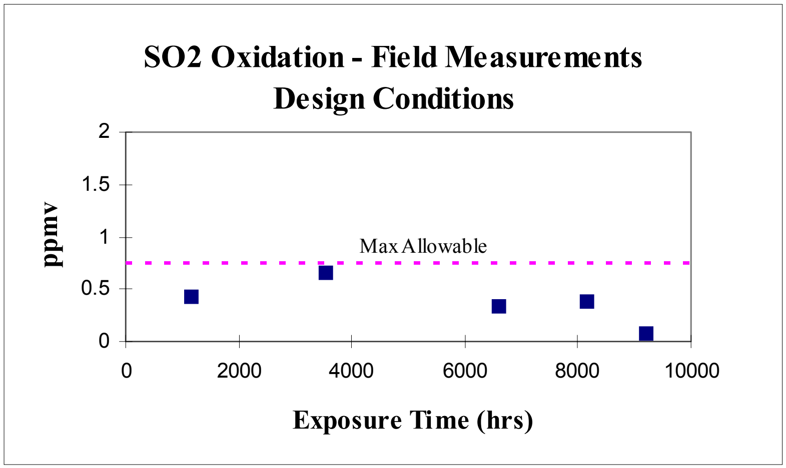

Figure 2

Pressure drop remained below the 4 inches H2O maximum for the duration of the demonstration.

Lab Performance Results

Field measurements were subject to more inaccuracies than measurements from a pilot scale laboratory reactor. The scatter in the field data makes it difficult to detect changes in catalyst performance. In order to more accurately measure the change in catalyst performance over time, full-sized catalyst samples were tested fresh and at the end of the demonstration in a pilot scale laboratory reactor. Such periodic testing is typical for SCR systems in order to assure proper operation and manage catalyst life. For a description of the pilot scale test, refer to "Quality Assurance of SCR Catalysts for the Southern California Edison 480 MW Power Generating Plants Through Laboratory and Field Performance Testing", Chris DiFrancesco, et. al., ICAC Forum '94.

The tests were performed at the design conditions. The catalyst pulled from the reactor was tested "as is" without any cleaning. Only the first two layers of catalyst were evaluated so that ammonia slip would be detectable (SV = 4164 hr-1). Ammonia slip increased over time from 0.7 - 1.4 ppmv, well below the 5 ppmv maximum, even with only two catalyst layers. (Figure 3)

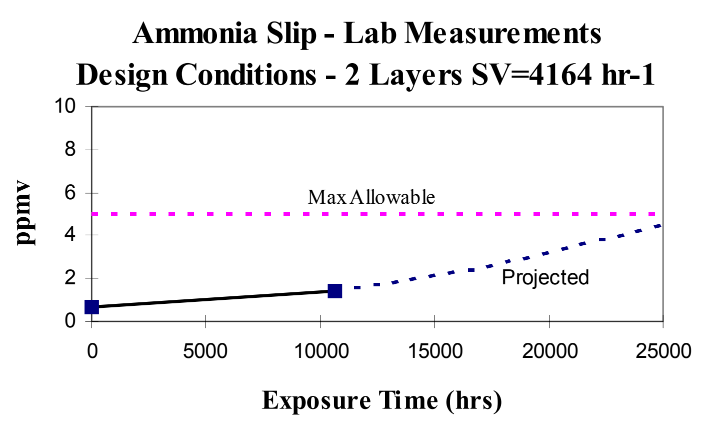

Figure 3

Based on this rate of change in performance, we predict that the ammonia slip for <u>two</u> layers of catalyst would remain below the 5 ppmv maximum for approximately an additional 15,000 hours.

Lab Chemical Analysis Results

Chemical analyses of field sample pulled at 10,600 hours was conducted by X-ray Fluorescence. It was determined that the decrease in performance over the duration of the demonstration was mainly due to a combination of arsenic (As) accumulation, surface masking by fly ash components (Ca, Fe), and alkaline metal accumulation (K). The graph below illustrates the observed increases in the X-ray intensities of these elements relative to the total X-ray intensities of the titanium catalyst base. (Figure 4)

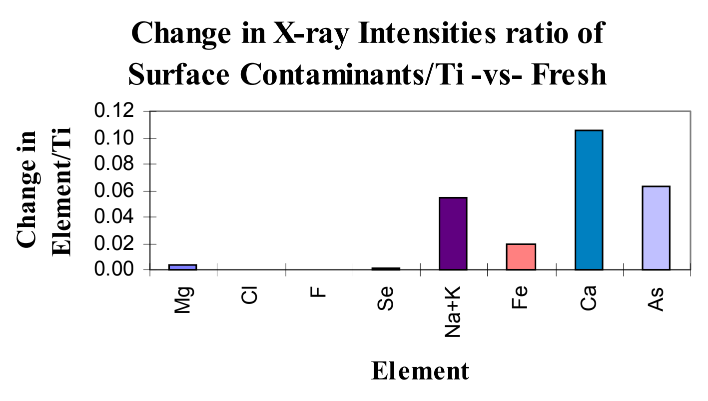

Figure 4

These performance deterioration factors are typical for coal fired applications and is consistent with the coal analysis in the appendix and the experience of Cormetech and its licensors. For a description of the deterioration mechanisms, refer to "Optimizing SCR Catalyst Design and performance for Coal-Fired Boilers", by Scot Pritchard, et. al., EPRI/EPA 1995 Joint Symposium on Stationary Combustion NOx Control.

B. Low Dust Summary (5,800 hours in operation)

Field Results

Operation time was limited on this reactor. Pressure drop was somewhat erratic (4 - 8 in H_2O) caused by plugging of the small pitched catalyst due to unexpected carry-over of large particulate to the "low" dust reactor. More than 30% of the catalyst was plugged with fly ash. This carry-over was due to the long duct runs of the test facility and a less than optimum flue gas take-off scoop. This situation would not be expected in a full scale unit.

Despite these operational issues, ammonia slip remained below 1 ppmv for the duration of the demonstration, well below the 5 ppmv maximum allowable slip. Similar to the high dust case, no change in ammonia slip over time was detectable in the field.

SO_2 oxidation rate remained well below the 0.75% maximum allowable rate for the duration of the demonstration. Similar to the high dust case, average SO_2 oxidation rate remained below 0.4% and no change in SO_2 oxidation rate over time was detectable.

Lab Results

As with the high dust reactor, fresh samples and samples removed at the end of the demonstration run were tested in the laboratory reactor. Although the reactor as a whole was 30% plugged, the particular samples tested were only 3% plugged. Ammonia slip increased over time from 0.6 - 1.0 ppmv, well below the 5 ppmv max. Based on this rate of change in performance, we predict that the ammonia slip would remain below the 5 ppmv maximum for more than 15,000 hours, excluding impact of the overall severe plugging.

Through chemical and physical property analyses, it was determined that the very slight decrease in performance over time was due mainly to a small amount of arsenic accumulation.

VI. CONCLUSIONS

For the high dust application, deNOx performance (catalyst deactivation), SO_2 oxidation, and pressure drop remained within design limits. Performance is expected to have lasted much longer than the duration of the demonstration even with only two-thirds of the reactor charge. Deterioration mechanisms and impact were consistent with expectations based on the coal composition fired.

Also, note that the low ammonia slip values achieved are consistent with current design practices (limit < 2-3 ppmv) to avoid fly ash contamination and excess air pre-heater maintenance. Design ammonia slip limits are unit specific depending on ash disposal method, sulfur content, and air pre-heater design.

For the low dust application, deNOx performance (catalyst deactivation) and SO_2 oxidation remained within design limits even with 30% of the catalyst plugged. Pressure drop increased significantly due to the plugging but was a result not realizing a truly low dust situation. If a truly low dust situation was realized, the catalyst performance, as in the high dust case, is expected to have lasted much longer than the duration of the demonstration.

APPENDIX

Boiler Type: Tangentially-Fired, Dry-bottom

Particulate Control: Hot and Cold-side Electrostatic Precipitator

Design Fuel Analysis:

C, wt %	67.80
H, wt %	4.60
S, wt %	2.90
N, wt %	1.40
Cl, wt %	0.25
Ash, wt %	9.50
Moisture, wt %	7.90
Oxygen, wt% (by diff.)	5.65

Actual Fuel Analysis from March 1993 to July 1995 Based on Monthly As-Burned Composites. Alabama Power Company Results, Dry Basis

Test	**Method**	**Units**	**Ave.**	**Std. Dev.**
Moisture, Total	ASTM D 3302	% by Wt	10.87	0.97
Ash	ASTM D 3180	% by Wt	9.30	0.63
Gross Caloric Value	ASTM D 3180	Btu/lb	13268	130
Sulfur, Total	ASTM D 3180	% by Wt	2.58	0.04
Sulfur, lb/MMBtu	ASTM D 3180	lb/MMBtu	1.95	0.31
Carbon	ASTM D 3180	% by Wt	74.82	0.81
Hydrogen	ASTM D 3180	% by Wt	5.00	0.07
Nitrogen	ASTM D 3180	% by Wt	1.25	0.03
Oxygen	ASTM D 3180	% by Wt	6.73	0.66
Carbon, Fixed	ASTM D 3180	% by Wt	52.83	1.31
Volatile Matter	ASTM D 3180	% by Wt	37.88	1.17
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Test	**Method**	**Units**	**Ave.**	**Std. Dev.**
Aluminum	ASTM D 3682	% by Wt	1.09	0.11
Antimony	ASTM D 3683	mg/kg	< 1.0	-
Arsenic	Sec. Chem. Acta. 44B	mg/kg	3.2	1.9
Barium	ASTM D 3683	mg/kg	40	18
Beryllium	ASTM D 3683	mg/kg	3	1
Cadmium	ASTM D 3683	mg/kg	< 1.0	-
Calcium	ASTM D 3682	% by Wt	0.24	0.03
Chlorine	ASTM D 4208	mg/kg	1767	812
Chromium	ASTM D 3683	mg/kg	19	4
Cobalt	ASTM D 3683	mg/kg	7	2
Copper	ASTM D 3683	mg/kg	9	2
Flourine	ASTM D 3761	mg/kg	56	27
Iron	ASTM D 3682	% by Wt	1.08	0.17
Lead	Sec. Chem. Acta. 44B	mg/kg	11.7	4.5
Lithium	ASTM D 3683	mg/kg	9	5
Magnesium	ASTM D 3682	% by Wt	0.06	0.02
Manganese	ASTM D 3683	mg/kg	24	4
Mercury	ASTM D 3684	mg/kg	0.07	0.04
Molybdenum	ASTM D 3683	mg/kg	7.78	4.33
Nickel	ASTM D 3683	mg/kg	15	2
Phosphorous	ASTM D 3682	% by Wt	0.02	0.02
Potassium	ASTM D 3682	% by Wt	0.20	0.06
Selenium	Sec. Chem. Acta. 44B	mg/kg	< 2	-
Silica	ASTM D 3682	% by Wt	2.27	0.19
Sodium	ASTM D 3682	% by Wt	0.06	0.02
Titanium	ASTM D 3682	% by Wt	0.06	0.01
Vanadium	ASTM D 3683	mg/kg	41	10
Zinc	ASTM D 3683	mg/kg	39	29

Design Flue Gas Composition:

N_2, vol %	73.29
O_2, vol %	3.01
CO_2, vol %	13.82
H_2O, vol %	9.61
SO_2, ppmv	2210
SO_3, ppmv	20
NOx, ppmv	400
Hcl, ppmv	104

Design Flyash Composition:

SiO_2, wt %	50.4
Al_2O_3, wt %	19.9
Fe_2O_3, wt %	18.1
TiO_2, wt %	1.0
CaO, wt %	4.2
MgO, wt %	1.0
K_2O, wt %	2.6
Na_2O, wt %	0.7
SO_3, wt %	1.4
P_2O_5, wt%	0.3
LOI, % (typ represents UC)	6.5

Design Particulate Loading: Average: High Dust - 8000 mg/Nm^3
Range: 6000 - 11,000

Average: Low Dust - 30 mg/Nm^3 Avg.