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LATEST NOX REMOVAL TECHNOLOGY FOR SIMPLE CYCLE POWER PLANTS

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Presented To

Power- Gen International; December 10- 12, 2002

Orange County Convention Center – Orlando, FL, USA

ABSTRACT

Hitachi has researched, developed and supplied various flue gas NOx removal technologies for thermal power plants throughout the world, greatly contributing to a cleaner environment. Anticipating the increased used of simple cycle combustion turbines to meet peak power demands the technology was broadened in the 1984 to include high temperature SCR DeNOx catalyst for these applications. After a brief demonstration, three (3) actual operating projects were developed and operated for approximate 5,000 hours at SCR operating temperatures ranging to 1,024 ^{0}F bulk flue gas temperature in the early 1990s. Catalyst substrate, configuration, formulation and ammonia oxidation rates are discussed and characterized. Comparisons with the low temperature catalyst and with material being used for this service today are made demonstrating the superiority of this new advanced high temperature catalyst.

INTRODUCTION

Today, with the competitive electric market and the requirements for a cleaner environment, generators are finding it attractive at times to build to meet seasonal demand or at least start with electric generating peaking simple cycle gas turbines. These units present a unique challenge to the environmental equipment suppliers.

The operating temperatures for the simple cycle NOx reduction system are higher than normally encountered with combined cycle power plants. This puts a severe burden upon the SCR catalyst integrity compared to the medium temperature SCR catalyst. High temperature catalyst is subjected to potentially rapid thermal degradation. Already high temperature SCR catalyst is reported as failing prematurely on both the east and west coast, the authors being aware of three plants total. The high operating temperatures complicate matters further in that the NOx reduction ammonia reagent is oxidized to create additional NOx, requiring both more catalyst and a higher ammonia reagent injection rate, again impacting the NOx. This NOx creation is impacted or catalyzed by the materials within the flue gas path. Thus the materials selected for the inside flue liner, the catalyst support structure, the catalyst modules and even the catalyst itself become important.

Included is actual operating experience for the advanced SCR catalyst discussed, both for testing in the high temperature zones of combine cycle plants and that of actual NOx reduction for simple cycle operation.

ARRANGEMENT

For simple cycle applications, the catalyst treats NOx in the exhaust gas that comes directly from gas turbine. As illustrated in Figure 1, the catalyst is installed in the reactor duct between gas turbine and stack. The gas temperature range where the catalyst is installed is around 900 to 1,100 degree F. For some units the original flue gas may be diluted with ambient air for temperature reduction or optimization to reduce the overall catalyst cost. These cases are excluded from this thesis as when a lower SCR operating temperature is used this allows lower temperature catalyst formulations. In cases where the regulations require CO reduction, a CO catalyst is normally installed upstream of the SCR catalyst and ammonia injection grid. This arrangement is used, as the CO catalyst is an oxidizing catalyst that is kept out of the inlet and outlet streams containing ammonia. This positioning prevents making more NOx by oxidation of the ammonia by the CO catalyst. In addition to the above, the flow leaves the turbine with a swirling motion that requires baffle plates and guide vanes installation upstream of SCR catalyst to assist in obtaining an even inlet flow distribution.

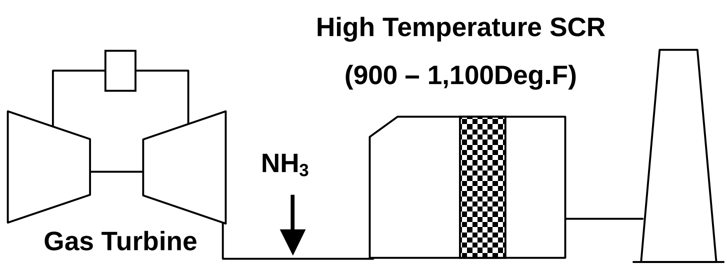


Figure 1 – Simple Cycle Schematic

CHEMICAL REACTIONS

In the high temperature gas flue, there are two types of chemical reactions as shown below: a reduction reaction, reaction (1), and two possible oxidation reactions, reactions (2) and (3). The reduction reaction reduces the NOx, which is required for emission regulations and the oxidation reactions oxidize the ammonia that is injected as the reagent for NOx reduction. Gas temperature, oxygen concentration, the material of casing and structure in the flue and the catalyst materials influence the oxidation reactions. In the high temperature case, the oxidation reactions have to be considered carefully to design the catalyst. From our test results and experience, the ammonia oxidation reactions occur in the flue gas and on the catalyst surface at higher temperatures. This causes a shortage of ammonia reagent to reduce the NOx and increases the amount of NOx (that which comes from ammonia) thereby increasing the required catalyst volume and the ammonia injection rate. Based on our data, the higher gas temperature is, the more ammonia oxidation takes place.

DeNOx Reduction Reaction: $4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$ **(1)**

NH_3 Oxidation Reactions: $4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$ **(2)**

$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O$ **(3)**

The oxidation reactions have different impacts upon the SCR design. When the ammonia oxidation proceeds to form NOx the catalyst design has to be adjusted to reduce this additional NOx and the injected ammonia has to be increased to add the necessary reagent. More ammonia reagent adds more NOx and the spiral to a larger system begins. The other oxidation reaction causes reagent loses but does not create NOx. Thus only the ammonia injection system is affected. Unfortunately, the authors cannot offer any guidance to determine which or in what combination, the reactions might occur.

TEMPERATURE CHARACTERISTICS

The advanced catalyst DeNOx efficiency varies with gas temperature and catalyst formulation. Figure 2 shows a comparison of efficiency based on gas temperature for both mid and the high temperature SCR catalyst. It is found that the advanced high temperature catalyst can perform at the high efficiencies of mid temperature range catalyst. This means that the advanced catalyst can use minimal cross-sectional flow area to perform the required duty. This advanced high temperature catalyst can cover the entire range of 572 degrees to 1,112^0 F with the peak performance at 842^0. Due to the increased cost of high temperature catalyst, however, it is normally applied over 900^0 F to perform NOx reduction. The higher the gas temperature, the more the catalyst supplier has to consider the NH_3 oxidation and the catalyst's performance period to select most efficient materials and formulation. The advanced high temperature catalyst is thus limited to bulk temperatures of 1,050^0 F with local temperatures not to exceed 1,100^0 to avoid excessive ammonia oxidation. The middle temperature catalyst shown below is considered to apply for combined cycle application. This catalyst can cover the performance in the lower temperature zone, from 900^0 F down to about 570^0 considering lower loads and sliding pressure operation.

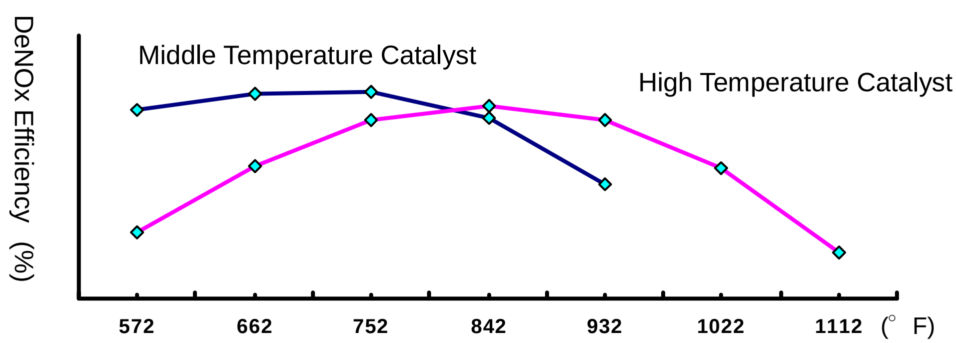


Figure 2 – Efficiency (Activity) with Temperature

OPERATIONAL RESULTS

Table 1 details actual operating flue gas conditions for the advanced high temperature catalyst. Plants A and B are combined cycle projects. Sample catalyst specimens were placed upstream of the HRSG in the hot gas stream directly from the gas turbine for future catalyst activity and durability analysis. As shown here, the sample catalyst in plant A was installed in 1981 about 20 years ago in anticipation of a more immediate demand for high temperature catalyst. Plant C is major Japanese utility demonstration short-lived pilot plant. Subsequently, two simple cycle plants were constructed that included high temperature DeNOx removal systems to treat gas turbine flue gas for two simple cycle projects, which are plants D and E that include the advanced high temperature catalyst for these simple cycle applications.

As shown in the Picture 1, the NOx removal system is located between the flue gas silencer and stack and designed with a horizontal flow reactor. The advanced catalyst performed well with gas temperatures, well over 900^0 F, in each plant, as shown in Table 1,

	Description	A plant	B plant	C plant	D plant	E plant
Gas Turbine	GT Type	F9B	F9E	-	F6B	F9E
	Output (MW)	141(Combined)	143(Combined)	-	41.7	127
	Fuel	NO.2 Oil	LNG	LNG	Town Gas	LNG
	Number of Units (Units)	1	1	1	2	1
SCR	Flue Gas Flow Rate (m3N/h)	977,000	1,012,000	603,000	415,880	1,201,500
Specification	Flue Gas Temperature (Deg.F)	1022	990	1067	993	1024
	Inlet Nox (ppm)	-	-	209 (5%O2)	50 (16%O2)	50 (16%O2)
	Outlet Nox (ppm)	-	-	<40 (5%O2)	<20 (16%O2)	<20 (16%O2)
	Outlet NH3 (ppm)	-	-	<10 (15%O2)	<20 (16%O2)	<20 (16%O2)
	Nox Removal Efficiency (%)	-	-	>80.9	>60	>60
	Date of Competion	1981	1987	1984	1992/1993	1993

Table 1

Picture 1 (E plant)

Figure 3 below is a sample commissioning result to show the dynamic characteristics of the advanced catalyst during start up prior and after ammonia injection. During start up, initial ammonia injection began at a gas temperature 572^0 F. After ammonia injection, the outlet NOx begins to decrease smoothly without a significant time lag and achieved the designated NOx outlet conditions within 3 minutes.

The outlet NOx concentration changed rapidly following the introduction of ammonia. The advanced catalyst was found able to withstand the rapid thermal transients of simple cycle service and also that it has a sufficiently rapid response to make it suitable to follow the load changes.

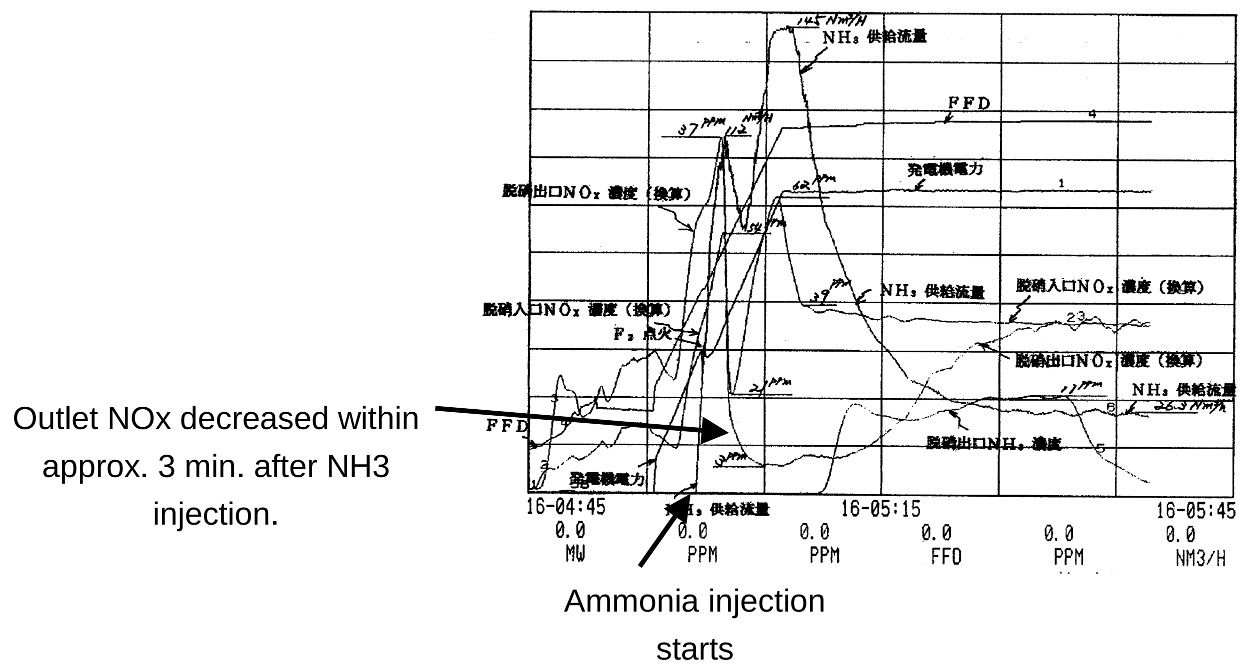
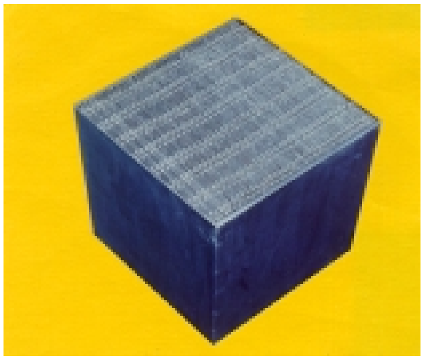


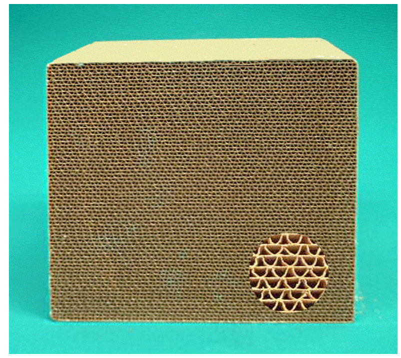
Figure 3 – Simple Cycle Start-Up Chart

ADVANCEMENTS FOR HIGH TEMPERATURE

Picture 2 shows the unit of mid temperature plate type catalyst. A certain number of catalyst plates are integrated and assembled in the unit box. The ingredients of the catalyst are based on TiO_2 with a substrate that is stainless steal meshed plate. The size of this unit is approximately 465 mm wide, 465 mm high and 500 mm deep where the width and depth dimensions can be adjusted to fit the cross section length of reactor and to perform NOx reduction requirement with low pressure



Picture 2 – Catalyst Unit



Picture 3 – Advanced Catalyst

drop. This catalyst is typically used for combined cycle and low gas temperature simple cycle applications.

Picture 3 shows the new advanced catalyst for high temperature simple cycle applications. The catalyst base is not stainless steel. In addition, rapid dispatching is critical for simple cycle peaking service: the advanced catalyst can withstand very rapid temperature changes in highly cyclic operation.

To meet such requirements, the newly developed advanced catalyst has a corrugated shape. This shape packs a large surface into a relatively small volume. The short length minimizes the catalyst's thermal resistance and thermal expansion. Also a ceramic material is used as a substrate for the catalyst. This, in the high temperature flue gas zone, minimizes the ammonia oxidation rate. The NH_3 oxidation activity of the advanced high temperature catalyst developed is considerably less than former high temperature catalysts.

The key for performance is the material used for the ceramic substrate. Titanium oxide and vanadium is the typical formulation. However vanadium contributes to ammonia oxidation. Tungsten was considered instead of vanadium but the formulation required a secondary additive to minimize ammonia oxidation. Figure 4 below shows the conceptual formulation of the advanced catalyst. This concept and the corrugated configuration achieved our requirements to get high specific surface area, to reduce the volume and achieve a short depth length, with low ammonia oxidation.

Figure 4 – Catalyst Structure

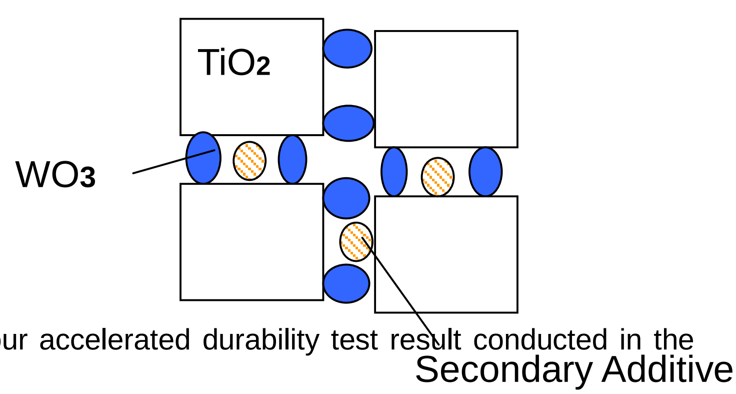


Figure 5 illustrates the results from a 100 hour accelerated durability test result conducted in the laboratory. The results indicate that the advanced high temperature catalyst formulation can perform longer than zeolite based high temperature catalyst. The accelerated zeolite deterioration was caused by the water concentration in exhaust gas that impacted the crystalline structure. Moisture in the flue gas would be the case for all fuel applications, especially when firing natural gas.

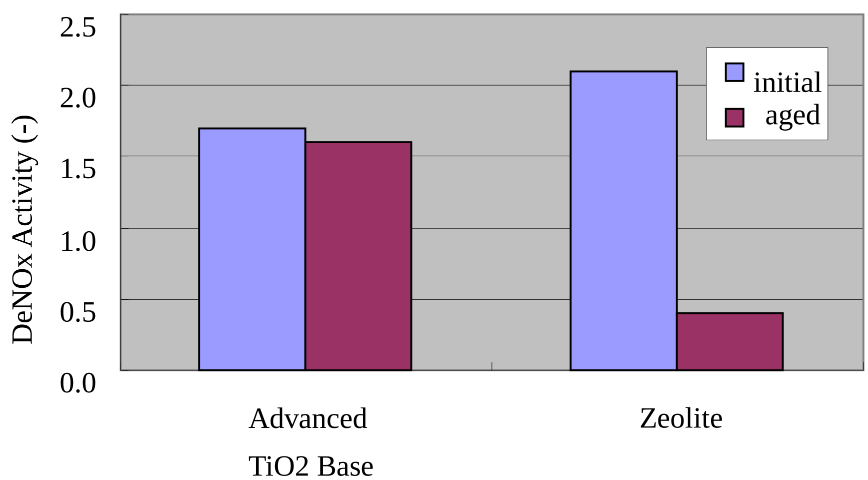


Figure 5 - Accelerated durability test

Figure 6 shows catalyst activity ratio versus gas temperature comparing the conventional type catalyst against the advanced catalyst. The sensitivity to temperature is almost same with the peak point at around 850^0 F. However, the advanced catalyst activity has approximately 1.5 times the activity of the conventional catalyst, which means that it reduces the catalyst volume considerably to minimize potential thermal expansion.

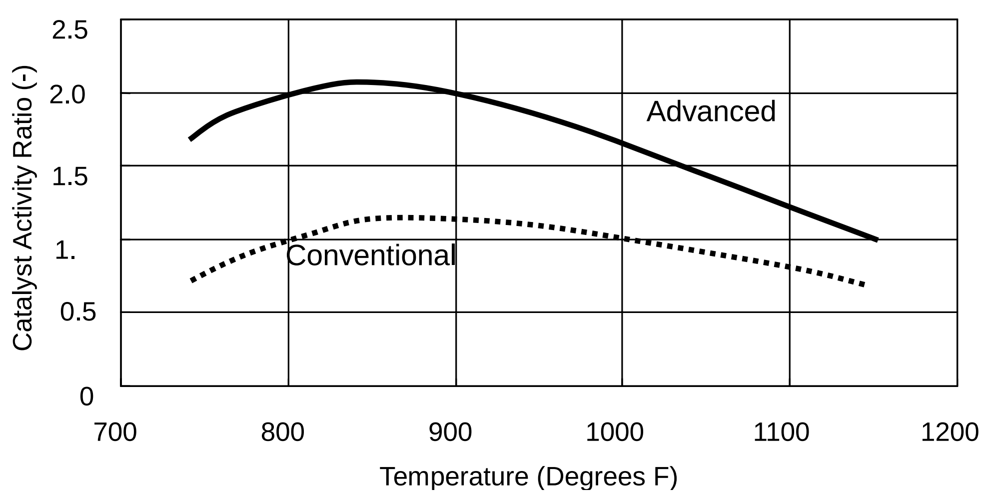


Figure 6 – Catalyst Activity with Gas Temperature

Figure 7 shows the durability of high temperature catalyst. As shown in the figure, performance is satisfactory for over 20,000 operating hours substantiating that the advanced catalyst has sufficient durability for commercial operation.

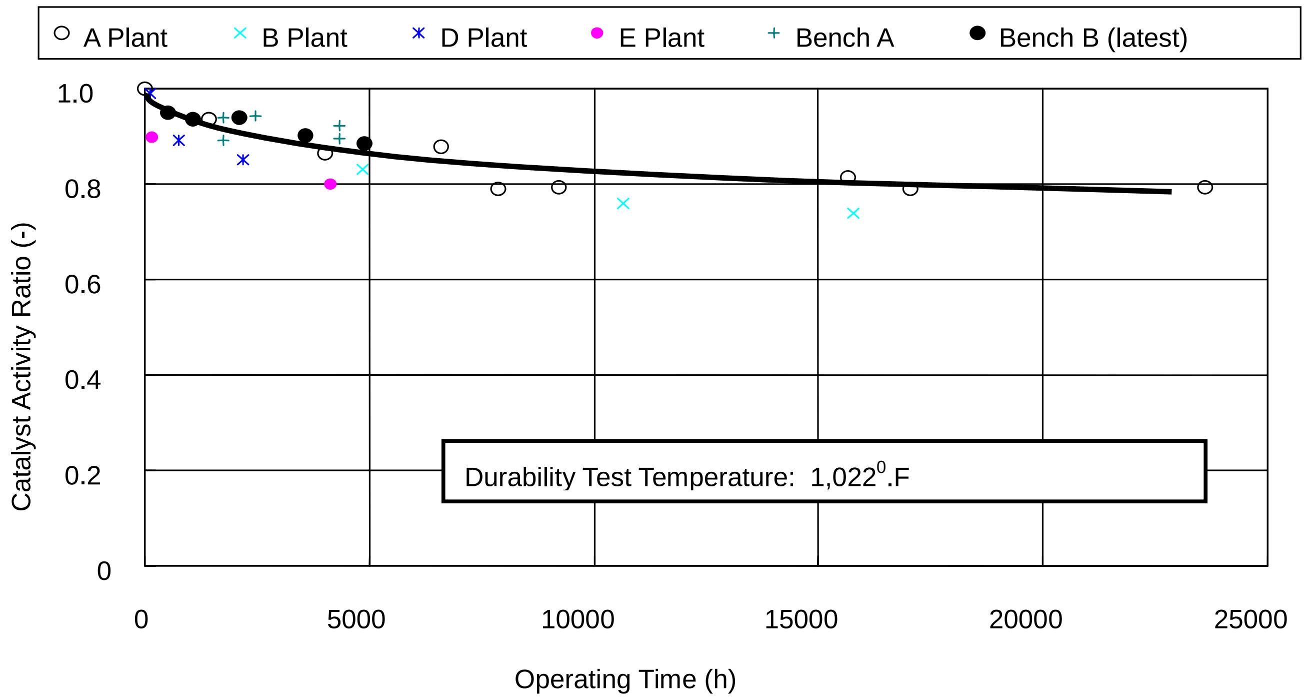


Figure 7 – Catalyst Activity Ratio with Operating Time

CONCLUSIONS

This paper has discribed a new advanced high temperature catalyst developed in the early 1990s for simple cycle applications. This catalyst has sufficient activity packed into a relatively small volume allowing for compact low pressure drop designs. It has considerable experience with proven durability at high temperatures, to 1,100^0 F and is only limited by the increase in ammonia oxidation ragtes with increasing operating temperature.