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Selective Catalytic Reduction Impact on Heat Recovery Steam Generator Design and Operation

JAMES S. DAVIS
Struthers Wells Corporation
P.O. Box 8
Warren, Pennsylvania 16365

G. C. DUPONTEIL
Struthers Wells, S.A.
3 rue La Boetie
75008 Paris, France

ABSTRACT

Selective Catalytic Reduction (SCR) is a post-combustion method to reduce the oxides of nitrogen (NO_x), present in flue gases such as gas turbine exhaust streams, to N_2 and water. It involves the injection of ammonia and the use of a catalyst module to promote the reaction to obtain high efficiency (60-86+%) NO_x reduction.

Several operating parameters can influence catalyst performance to include temperature, gas flow distribution, presence of sulfur compounds and catalyst age. This paper examines the impact of a SCR integration in a gas turbine heat recovery steam generator (HRSG) design/operation. Limitations on HRSG load and following capabilities, effect on capital cost and overall performance and current SCR system experience represent a number of areas that are examined.

INTRODUCTION

In increasing locations, the ability to comply with air quality standards for nitrogen oxides (NO_x) and ozone (O_3) is becoming an important siting problem for new cogeneration and power generating projects. NO_x is a chemical precursor to photochemical smog (ozone, peroxyacyl nitrates and related compounds) as shown by the following reactions:

$$\begin{array}{llll} 2\ NO + O_2 & \rightarrow & 2\ NO_2 & \\ NO_2 + h\nu & \rightarrow & NO_2^* & NO + O \\ O + O_2 & \rightarrow & O_3 & \\ O_3 + HC + NO_2 & \rightarrow & \text{Photo Chemical Smog} & \end{array}$$

Nitrogen oxides formed in combustion processes are usually related to two mechanisms:

1. "Thermal NO_x" - thermal fixation of atmospheric nitrogen in the combustion air.

2. "Fuel NO_x" - conversion of the chemically bound nitrogen contained in the fuel.

For natural gas firing, nearly all NO_x emissions are thermal NO_x. With residual oil, crude oil and other fuels, the contribution from fuel bound nitrogen can be significant.

In many locations, the use of gas turbines with heat recovery boilers is a very efficient and cost effective approach for cogeneration and power generation (1). In gas turbine applications, two methods can currently be used to reduce the NO_x (typically 120-250 ppm) emissions in the exhaust gas. These methods can be classified as:

1. Water or steam injection into the gas turbine combustor to achieve a flame temperature reduction. This reduces the thermal fixation of atmospheric nitrogen. Achievable NO_x emissions with method are in the range of 30-100 ppm.

2. Selective Catalytic Reduction (SCR) uses injected ammonia to react preferentially with NO/NO_2 in the presence of a suitable $DeNO_x$ catalyst to form water and nitrogen. Combined with steam injection, NO_x emissions can be reduced to the levels of 3-10 ppm.

Additionally, a CO catalytic convertor can be used to reduce the carbon monoxide emission levels. A number of past references (2,3,4) have discussed SCR designs and operation in specific gas turbine, combined-cycle, power plants. However, for cogeneration applications, the variation of the HRSG operating conditions can differ significantly from a gas turbine power plant design.

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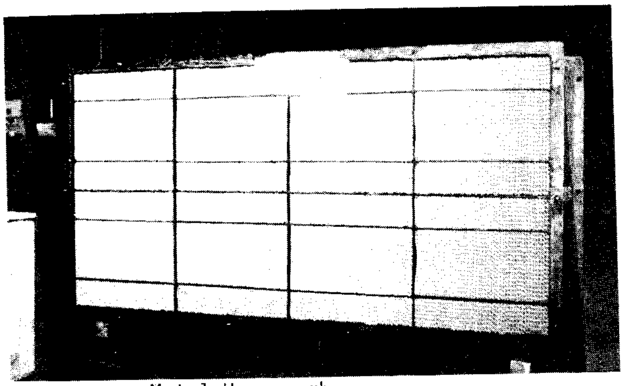
SCR: GAS TURBINE APPLICATIONS

The characteristics of an efficient, reliable SCR catalyst can be identified by:

1. High activity and high selectivity to the NO_x-NH_3 reaction.
2. Resistant to large thermal gradients, particularly as experienced in gas turbine startups.
3. Low pressure drop (38 - 76 mm H_2O).
4. Resistant to SO_x and other contaminant poisioning.
5. Long catalyst life (> 2 years) at required NO_x removal efficiencies.

The metal honeycomb and plate type SCR catalysts are the design of choice to provide high thermal stability and high surface area/ volume ratios. In general, catalysts composed of vanadium oxide (V_2O_5) or V_2O_5 and titanium dioxide are highly resistant to sulfation and related loss in activity.


Metal Honeycomb
(Courtesy: Hitachi-Zosen)

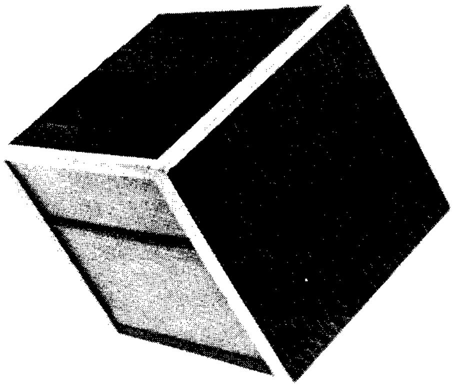


Plate Type
(Courtesy: Hitachi Ltd.)

High NO_x removal efficiencies (80-90%) require uniform distribution of the NH_3 reactant across the HRSG "gas-flow cross section." Typical locations of the NH_3 injection grid (AIG) can be characterized as:

1. In gas turbine exhaust duct (Option A-Reference: Figure 1). Suitable only for a HRSG without supplemental firing. This location provides the minimum cross section for the NH_3 injection grid.
2. In Option B, the AIG is located upstream of either the superheater or HP boiler coils. This design further complicates the SCR integration in the HRSG design in that both the catalyst and AIG must be integrated within tube rows. The one potential benefit is a longer mixing zone.
3. Prior to SCR catalyst module (Option C). Located upstream of SCR catalyst modules and mixing zone, this approach provides the simplest integration for supplementary fired HRSG designs.

It is the objective of any ammonia injection system to:

1. Minimize NH_3 injection rates.
2. Have small NH_3 leakage (or slip) rates to the environment.
3. Maintain required NO_x removal efficiency.

For designs including a CO converter, the AIG should be located downstream of the CO catalyst modules. This arrangement avoids oxidation of a portion of the ammonia to NO_x. Control of the ammonia injection consists of both feed-forward and feed-back control loops as illustrated in Figure 1-A.

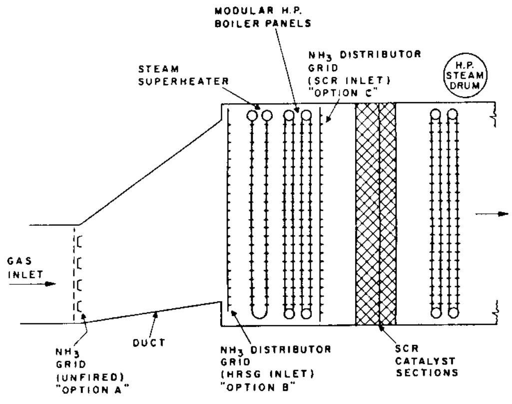


FIGURE: 1

HRSG / SCR INTEGRATION

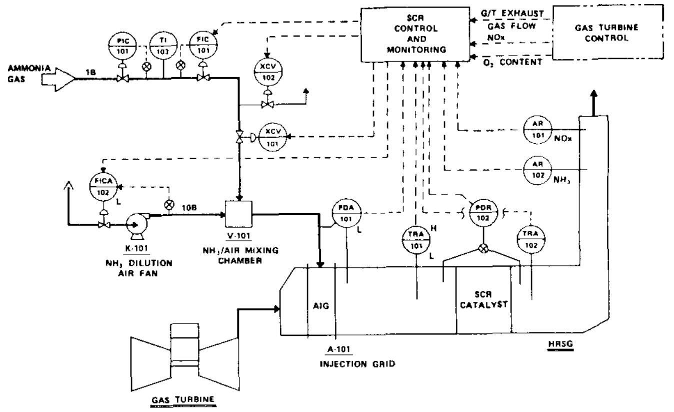


FIGURE 1A: NH_3 INJECTION CONTROL SYSTEM

OPERATING FLEXIBILITY

In many cogeneration applications, significant load-following requirements are imposed on the HRSG-SCR design. Load-following requirements can be related to:

1. Need to match a variable process steam demand.

2. Need to replace capacity of another steam generation unit during an outage.

3. Need to meet a peak power demand.

To avoid catalyst degradation, the SCR catalyst is operated in the temperature range of 300 - 410 deg. C (SO_x free gas). To meet this operating criteria, the SCR needs to be located within the high pressure (HP) boiler section of a typical single or multi-pressure, HRSG. (Reference: Figure 1). In general the temperature drop of the exhaust gas across each boiler tube row decreases as the gas stream moves further into the HP boiler section. As the exhaust gas is cooled in the HP boiler, the temperature difference available as the driving force for heat transfer also is decreasing. This effect reduces the variation of gas temperature as the gas moves through the HP boiler during load variation and helps to maintain the catalyst within the proper operating temperature range.

In any case, the selected location of the SCR catalyst must insure:

1. Catalyst is operated below a maximum temperature to prevent rapid degradation and possible sintering.

2. Catalyst is operated above a minimum temperature to provide the required NO_x removal efficiency.

Figures 2 and 3 A/B provide a profile of the exhaust gas temperature as function of the boiler tube row location. For these simple applications, the HRSG operating requirements can be defined as:

Case A (Figure 2): HRSG is a multi-pressure level design with the ability to meet a wide process steam flowrate variation. HP steam generation can be varied as follows:

A) Unfired operation: 61,000 kg/hr.
B) Normal fired operation: 120,000 kg/hr.
C) Maximum fired operation: 150,000 kg/hr.

Operating pressure for the HP boiler is 59.8 kg/cm^2. Location of SCR was selected between rows "N+6" and "N+7". Note the general decrease in gas temperature variation through the HP boiler between operating modes.

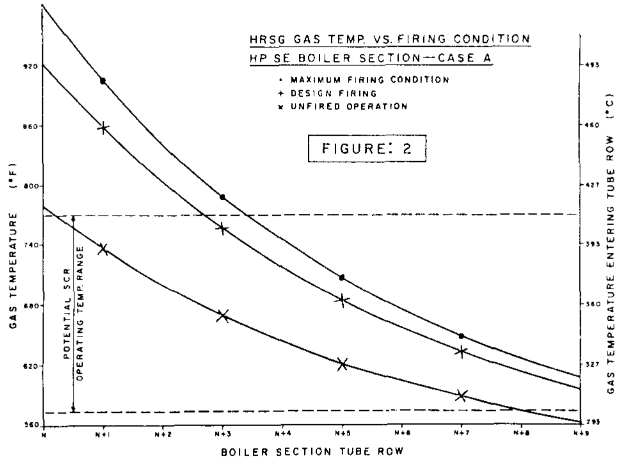


FIGURE: 2

Case B (Figures 3 A/B): This unique application consists of a two gas turbine and two interconnected HRSG units. The first HRSG (SE design) is a dual-pressure unit design for power generation. The second HRSG (SI design) generates 80% quality steam at 70.3 kg/cm^2 for use in enhanced heavy oil recovery production. The output of the SI HRSG is controlled by diverting gas turbine exhaust flow to the SE HRSG, thus allowing the SI boiler to operate in a turndown condition. The SE HRSG is designed to handle a 1.7/1 variation in gas flowrate. The HP boiler section of the SE unit is designed to operate as a sliding pressure over the range of 35.3 to 55 kg/cm^2. The sliding pressure operation provides a constant steam volumetric flowrate to the steam turbine and this maintains steam turbine efficiency over the range of operating conditions. The SCR unit is located:

(A) SI boiler: Between rows 5 and 6.
(B) SE boiler: Between rows 4 and 5.

These locations provide the required temperature range for the SCR over the various boiler operating conditions. Proper design of the SCR must include a detailed optimization of SCR costs, operating pressure drop and module sizing. Design and operating considerations for the HRSG/SCR integration are summarized in Table 1 found at the end of this paper.

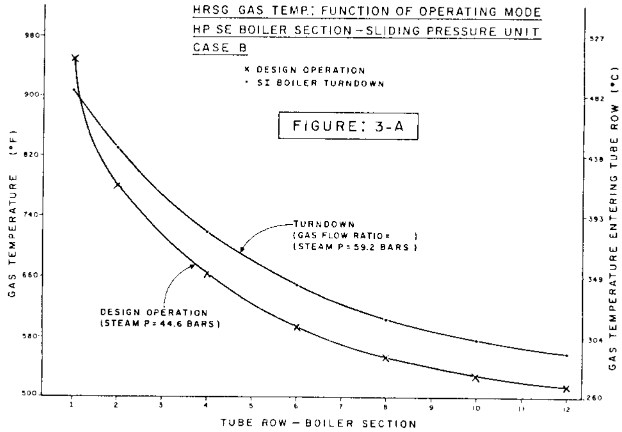


FIGURE: 3-A

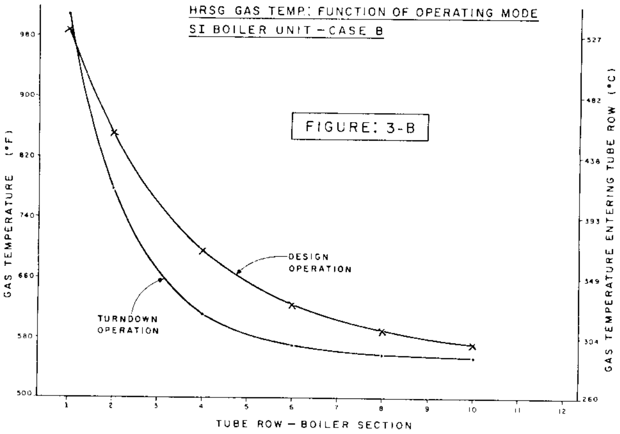


FIGURE: 3-B

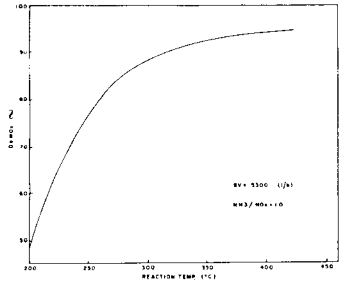
CATALYST PERFORMANCE CHARACTERISTICS

Major work by the SCR catalyst manufacturers has significantly improved the $DeNO_x$ catalyst capabilities. Improvements over the early power plant catalysts have included:

1. Ability to handle higher SO_x concentrations and dust loading.
2. Lighten catalyst weight.
3. Improved catalyst activity at lower temperatures.
4. Lower pressure drop requirements.

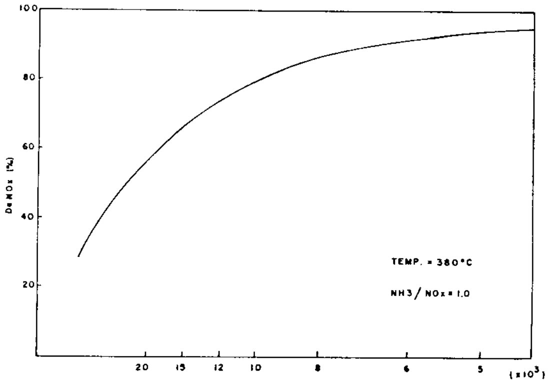
Operating temperature is a prime design variable for attainable NO_x removal efficiency. As illustrated in Figure 4, increasing $DeNO_x$ efficiency from 80 to 90% results in a significant increase in the minimum operating SCR temperature. Increasing $DeNO_x$ efficiency thus decreases the allowable temperature window for SCR operation. This reduced temperature window makes determination of the SCR location in the HRSG more complicated.

Increased residence time in the catalyst modules increases the No_x removal efficiency. A careful evaluation of space velocity, incurred pressure drop, and overall cost must be undertaken to provide the most cost effective design. Figure 5 illustrates a typical relationship of space velocity to catalyst efficiency.



EFFECT OF TEMPERATURE ON EFFICIENCY [A]

FIGURE 4



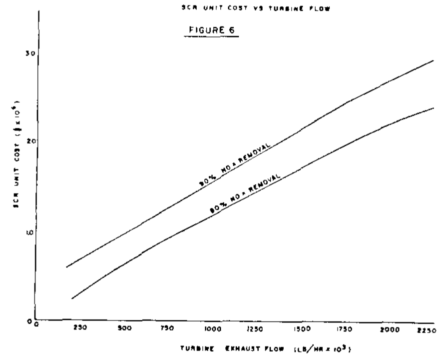
EFFECT OF SPACE VELOCITY ON EFFICIENCY [A]

FIGURE 5

As the SCR efficiency is increased, the required catalyst volume is significantly larger and the NH_3/NO_x ratio must also increase. Thus high NO_x removal efficiencies (85+%) result in:

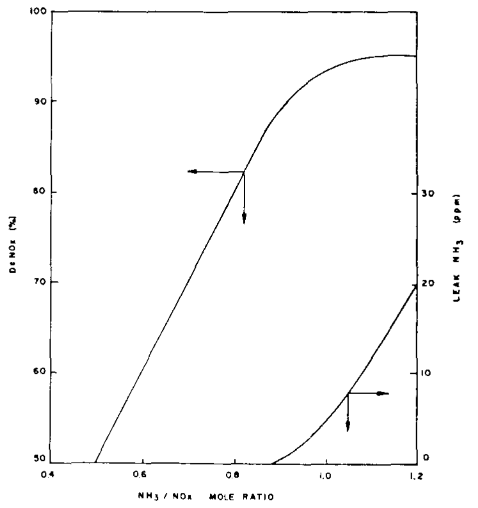
1. Higher system costs (Reference: Figure 6. Costs presented include AIG and control system, reactor casing and catalyst modules.)
2. Increased system pressure drops resulting from larger SCR catalyst volume.
3. Higher NH_3/NO_x injection ratio and greater NH_3 leakage to the atmosphere. (Figure 7 shows the impact of NO_x efficiency on these design parameters.)

(A) Figures 4 and 5: Courtesy Hitachi Zosen Corp.



SCR UNIT COST VS TURBINE FLOW

FIGURE 6



EFFECT OF NH3/NOx RATIO ON EFFICIENCY AND LEAKAGE NH3

FIGURE 7

The need for a SO$_x$ resistant SCR catalyst for maintaining high activity has been previously discussed. One added operating concern, due to the presence of SO$_x$, is potential heat transfer surface fouling downstream of the SCR unit. DeNO$_x$ catalyst will oxidize a portion of the SO$_2$ and SO$_3$. The small quantities of sulfur trioxide can react with the slip ammonia leakage to form ammonium bisulfate or ammonium sulfate. Both materials can deposit on the colder downstream heat transfer coil. The deposition of these compounds can be predicted by a thermodynamic phase equilibrium analysis. Deposition temperatures in terms of metal surface temperatures can be calculated as a function of the ammonia leakage and SO$_3$ concentrations. SCR catalyst for gas turbine applications are being designed to produce a minimal conversion of SO$_2$ to SO$_3$. The addition of a CO converter to the HRSG can greatly enhance the fouling problems due to oxidation of sulfur dioxide to SO$_3$.

SUMMARY

The successful integration of SCR systems into HRSG designs require the analysis of several design parameters. The expected range of gas turbine/HRSG must also be closely examined to determine impact on SCR design. As noted in Table 2, several SCR systems have been operated successfully in gas turbine power plants. The long term success of SCR systems in cogeneration applications will require close attention to design detail.

TABLE 1

SCR DESIGN CONSIDERATIONS

1. NO$_x$ Removal Efficiency (80-90% Typical)
    - . Variation of NO$_x$ as function of gas turbine operation
2. Operating Range Requirements
    - . Optimize catalyst cost/effect of operating ΔP.
    - . Selection of gas temperature "window".
3. Resistance to Thermal Shock
4. Gas Stream Contaminants
    - . Sulfur compounds - ammonium bisulfite formation
    - . Dust loading
    - . Catalyst poisons
5. Design/Location of NH$_3$ injection
    - . Unfired designs
    - . Fired designs
    - . Flow modeling
    - . Adequate distribution
6. Commercial Warranty
    - . Effective Catalyst Life and Performance Guarantees

TABLE 2

SCR EXPERIENCE - GAS TURBINE HRSG

SCR SUPPLIER	CUSTOMER	TOTAL GAS FLOWRATE (NM3/HR)[FUEL]	DENOX EFF. %	ON-STREAM DATE
HITACHI LTD.	JAPANESE NATIONAL R.R. KAWASAKI 1	1,024,000 [KEROSENE]	80	1981
HITACHI ZOSEN CORPORATION	SUMITOMO RUBBER	43,700 [OIL]	80	1984
HITACHI LTD.	MITI/MOON LIGHT PLT	603,100	84	1984
MITSUBISHI H.I.	TONOKU ELECTRIC POWER NIGATA	8,190,000 [LNG]	< 40 PPM NOX OUTLET	1984/1985
JOHNSON MATTHEY	AMERICAN COGENERATION	208,300 [OIL]	-	1984/1985
HITACHI ZOSEN	TOKYO ELECTRIC POWER	17,500,000 [LNG]	90	1985
JOHNSON MATTHEY	UNITED AIRLINES	196,400 [NAT. GAS]	-	1985
JOHNSON MATTHEY	UNION OIL	343,600	-	1986
HITACHI LTD.	KYUSHU EPCO/ SHINOHITA 1	(700 MWE) [LNG]	-	1986
HITACHI ZOSEN	CHUBA ELECTRIC/ YOKKAICHI	4,200,000 [LNG/LPG]	90	1986

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   C. Johnson Matthey, Inc.