

B.15 SELECTIVE CATALYTIC REDUCTION^{28,29,30}

B.15.1 Background

Selective catalytic reduction (SCR) is an add-on NO_x control technology for process gas streams with significant oxygen (O₂) content. An SCR consists of a catalyst surface, reactor housing and support, ammonia (NH₃) system (storage tank, vaporizer, injection grid, dilution air system, and control system), CEMS, and control system. The control efficiency achieved for NO_x ranges from approximately 70 to 90 percent depending on the application. In SCR, NH₃ is injected into the inlet gas stream upstream of the catalyst bed; in the catalyst bed, the NH₃ reacts with NO_x in the presence of O₂ to form nitrogen (N₂) and water (H₂O). The NO_x reduction efficiency is controlled by the ratio of NH₃ injected to the amount of NO_x in the gas stream (NH₃/NO_x), the catalyst material and condition, the space velocity, and the catalyst bed operating temperature. Increasing the NH₃/NO_x ratio increases the level of NO_x emission reduction but may also result in higher NH₃ slip levels. (Ammonia slip occurs when too much NH₃ is injected and the unreacted portion is emitted in the outlet stream from the SCR.) In general, the outlet concentration of NH₃ from the SCR should be held to less than 5 ppmv. Side reactions may produce ammonium sulfate and ammonium bisulfate byproducts when SO₃ is also present; SO₂ in the process gas stream oxidizes to SO₃ in some catalysts. These byproducts may cause plugging and corrosion of downstream equipment. The load applied to the process unit (e.g., gas turbine or some stationary internal combustion engines) affects both the exhaust temperature and the NO_x emission levels from the process, and various exhaust temperature and NO_x swings may pose problems for the SCR unit. The complexity of the NH₃ injection control system increases with fluctuations in load.

The catalyst is arranged in a series of two to four beds or layers. Catalysts may include base-metal oxides, precious metals, or zeolite. Optimum operating temperatures for SCR units using a base-metal oxides catalyst range from 600° to 750°F, depending on catalyst type; operating temperatures for platinum catalysts are lower than this range. Zeolite catalysts require an operating temperature of 600° to 900°F, and as high as 1100°F. Typically, the optimum performance of each SCR catalyst lies within a narrow temperature range of ±50°F. Below this range, catalyst activity is reduced and NH₃ slip increases. Above the range, NH₃ may be oxidized to form NO_x, which is counter to the control device purpose.

As catalyst activity declines, additional catalyst should be installed; as deactivation continues, the catalyst can be replaced one layer at a time. Sufficient catalyst volume must be provided to allow for inevitable catalyst deactivation. Catalyst deactivation may average up to 20 percent over a two-year period depending on the application. The use of fuels other than natural gas may mask or poison the catalyst. If diesel or other fuels are used, a bed guard upstream of the catalyst bed should be used to collect heavy hydrocarbons that would deposit on or mask the catalyst. Zeolite catalyst is recommended for diesel fuel processes to minimize masking and poisoning and to limit NH₃ byproduct side reactions. Soot blowing, vacuuming, or superheated steam application may be conducted periodically to remove particulate or masking from the catalyst.

Space velocity (gas flow rate divided by the catalyst bed volume) is an indicator of residence time in the catalyst bed. Lower space velocities give higher residence times and higher NO_x reduction rates.

B.15.2 Indicators of SCR Performance

The primary indicators of SCR performance are outlet NO_x concentration, NH₃/NO_x ratio, catalyst bed inlet temperature, and the catalyst activity. Other parameters that can indicate SCR performance include the outlet NH₃ concentration, catalyst bed outlet temperature, inlet gas flow rate, sulfur content of the fuel combusted, and the pressure differential across the catalyst bed. Table B-15 lists these indicators and illustrates potential monitoring options for SCR.

Outlet NO_x concentration. The most direct single indicator of the performance of a SCR is the NO_x concentration at the outlet of the unit.

NH₃/NO_x ratio (NH₃ injection rate). The NH₃ injection rate should increase or decrease with changes in inlet NO_x levels due to varying process load. With increasing NH₃/NO_x ratio, the NO_x level and the NH₃ slip remain fairly constant and the SCR reduces NO_x emissions; however, above a certain value or ratio, the NH₃ slip begins to increase. Limiting the amount of NH₃ slip is important to limit NH₃ emissions from the SCR and to suppress reactions of the additional NH₃ with SO₂ and SO₃, if present, to form ammonia salt byproducts.

Catalyst bed inlet temperature. The temperature at the inlet to the catalyst bed provides a good indication of catalytic reduction performance because it indicates that the gas stream is at sufficient temperature to initiate reduction of NO_x on the catalyst. Too high of an inlet temperature (i.e., of the process gas stream) may cause NO_x generation in the SCR rather than NO_x reductions.

Catalyst activity. Catalyst deactivation will result in increases in NO_x emissions and NH₃ emissions (ammonia slip). Catalyst activity should be checked periodically and/or the catalyst or portion of the catalyst should be replaced periodically.

Outlet NH₃ concentration. NH₃ in the outlet stream is an indicator that too much NH₃ is being injected or that reduction of NO_x is not occurring on the catalyst.

Catalyst bed outlet temperature. The bed outlet temperature provides an indication that reduction is occurring on the bed. Maintaining the operating temperature in the catalyst bed is crucial in avoiding NO_x generation at high temperatures. In general, lower operating temperatures mean lower NO_x emissions, to a minimum temperature below which NO_x reduction does not occur. Increases in the operating temperature of the SCR may cause an increase in NO_x generation rather than NO_x reductions. Also, there is a maximum temperature above which the catalyst begins to sinter; monitoring the bed outlet temperature will ensure that the temperature within the bed does not exceed its working limit.

Inlet gas flow rate (Space velocity). Control efficiency is a function of the space velocity (similar to residence time), and space velocity is a function of the gas flow rate. As flow rate increases, the space velocity increases and control efficiency declines. Decreases in flow rate typically mean an increase in control efficiency.

Sulfur content of fuel. Processes that use sulfur-containing fuels should include a limit on the sulfur content. Higher sulfur content may result in increased formation of ammonia salt byproducts.

Pressure differential across catalyst bed. An increase in pressure differential over time may provide an indication that particulate matter (PM) is accumulating on the catalyst bed. Periodic blowing, vacuuming, or steaming of the bed is necessary to remove accumulated PM.

B.15.3 Illustrations

The following illustration presents an example of compliance assurance monitoring for SCR:

15a: Catalyst bed temperature, outlet NH₃ concentration, and catalyst activity.

B.15.4 Bibliography

TABLE B-15. SUMMARY OF PERFORMANCE INDICATORS FOR SCR_s

Parameters	Performance indication	Approach No.	1	2	3	4	5
		Illustration No.		15a			
		Example CAM Submittals					
		Comment					
Primary Indicators of Performance							
Outlet NO _x concentration	Direct measure of outlet concentration. Best single indicator of SCR performance.		X				
NH ₃ /NO _x ratio (NH ₃ injection rate)	Amount of NH ₃ injection should be stoichiometrically based on NO _x concentration in the inlet stream. Want to maximize the ratio without increasing NH ₃ slip.				X	X	X
Catalyst bed inlet temperature	Indicator that bed inlet is of sufficient temperature to initiate reduction. Also an indicator that bed inlet temperature is not too high for catalyst longevity. High temperatures encourage generation of NO _x rather than a reduction in NO _x .				X	X	X
Catalyst activity	Periodic check of catalyst activity gives an indication of catalyst fouling or masking. Must periodically clean and/or replace catalyst to ensure reduction is occurring.			X	X		
Other Performance Indicators							
Outlet NH ₃ concentration	Indicator that NH ₃ injection rate is too high. Must adjust to reduce NH ₃ slip.			X			
Catalyst bed outlet temperature	Indicator of the level of reduction that is occurring in the catalyst bed and that temperature does not exceed design limits of catalyst. Too high a temperature may encourage generation of NO _x rather than a reduction in NO _x .			X	X	X	X
Pressure differential across catalyst bed	Indicator of bed fouling or plugging. Increase in pressure differential indicates that bed is becoming fouled or plugged. Changes in pressure differential are likely to be gradual.						X
Comments: None.							

CAM ILLUSTRATION

No. 15a. SELECTIVE CATALYTIC REDUCTION FOR NO_x CONTROL

1. APPLICABILITY

- 1.1 Control Technology: Selective catalytic reduction [065]
- 1.2 Pollutants
 - Primary: Nitrogen oxides (NO_x)
 - Other: Nitric acid (HNO₃), ammonia (NH₃)
- 1.3 Process/Emission units: Gas turbines, internal combustion engines (ICE), process heaters, nitric acid production units, and boilers

2. MONITORING APPROACH DESCRIPTION

- 2.1 Indicators Monitored: Catalyst bed temperature, outlet NH₃ concentration in flue gas (NH₃ slip causes ammonia salt fouling of the catalyst), and catalyst activity.
- 2.2 Rationale for Monitoring Approach
 - Catalyst bed temperature: Indication that the reaction is occurring in the catalyst bed; too high a bed temperature may generate NO_x rather than reduce NO_x.
 - Outlet NH₃ concentration: Indication of NO_x reduction or indication that NH₃ feed is too high; fouling of the catalyst is caused by ammonia salt byproducts, the formation of which can be avoided by limiting ammonia slip and limiting fuel sulfur content.
 - Catalyst activity: Indication of the catalyst's ability to promote the reaction between NO_x and NH₃.
- 2.3 Monitoring Location
 - Catalyst bed temperature: Outlet to the catalyst bed.
 - Outlet NH₃ concentration: NH₃ monitored at outlet duct of catalyst bed.
 - Catalyst activity: Removal of a small portion of catalyst for testing.
- 2.4 Analytical Devices Required: Thermocouples or other temperature instrumentation, NH₃ CEMS (other methods and instruments may be unit-specific).
- 2.5 Data Acquisition and Measurement System Operation
 - Frequency of measurement:
 - Catalyst bed temperature: Measure continuously.
 - Outlet NH₃ concentration: Measure continuously.
 - Catalyst activity: Measure periodically.
 - Reporting units:
 - Catalyst bed temperature: Degrees Celsius or Fahrenheit (C or F).
 - Outlet NH₃ concentration: Parts per million by volume (ppm_v) NH₃.
 - Catalyst activity: Percent active compared with new catalyst (or other as appropriate).
 - Recording process:
 - Catalyst bed temperature: recorded automatically on strip chart or data acquisition system.

- Outlet NH₃ concentration: recorded automatically on strip chart or data acquisition system.
- Catalyst activity: manually recorded in SCR maintenance log.

2.6 Data Requirements

- Baseline catalyst bed temperature, outlet NH₃ concentration, and catalyst activity measurements concurrent with emission test.
- Historical plant records of catalyst bed temperature, outlet NH₃ concentrations, and catalyst activity measurements.

2.7 Specific QA/QC Procedures

- Calibrate, maintain, and operate instrumentation using procedures that take into account manufacturer's recommendations.

2.8 References: _____

3. COMMENTS

None.