

Introduction



Kittiwake Procal's expertise in the measurement of nitrogen oxide (NO_x) gases make the company one of the leading providers of CEMs equipment for use with Selective Catalytic Reactor (SCR) systems. When nitrogen oxides (NO_x) and volatile organic compounds (VOCs) enter the atmosphere, they react in the presence of sunlight to form ground-level ozone, which is the major constituent of smog. Since the introduction of the "Clean Air Act in 1967" and subsequent amendments in 1970, 1977 and most recently in 1990 there has been a drive to install and retro-fit SCR systems to reduce NO_x emissions. An SCR is an important and valuable capital equipment asset for use in emissions reduction that when installed on a power utility can reduce NO_x emissions by 70-95%.

Procal with its in house design and research department is able to provide site specific installation drawings and service requirement documents for the P2000 analyser so that it can be installed trouble free on existing SCR systems. Although, SCR systems are usually identified with large utility boilers, industrial boilers, and municipal solid waste boilers they have also been applied to marine diesel engines, diesel locomotives, gas turbines, and automobiles.

SCR and marine engine NO_x emission regulations



As part of the Kittiwake Group of companies Kittiwake Procal has adapted its successful P2000 analyser for in-situ CEMs marine diesel engine applications. The "1997 Protocol" agreement produced an amendment to the the "International Convention on the prevention of pollution from ships" known as MARPOL regulated by the International Maritime Organisation (IMO). Annex VI – "Regulations for the Prevention of Air Pollution from Ships" regulates fuels and exhaust gas emissions setting limits for NO_x and SO_x from ships, mobile off-shore drilling rigs and other oil industry platforms. A group of tiered standards have been set in which Tier III standards require dedicated NO_x emission control technologies such as selective catalytic reduction. Procal 2000's emissions monitoring system is approved for the analysis of exhaust gases from the engines and boilers of ships and offshore rigs. Robust and with proven reliability, up to six gases can be measured including NO_x , SO_2 and CO_2 .

With high penalties for non-compliance the exhaust gases from the combustion of residual and distillate fuels can be analysed by the P2000 so that compliance can be confirmed in port, in Emissions Control Areas and in international waters. Materials of construction are also ideally suited to the marine environment.

Whilst the pace of change has created uncertainty and appears to have pushed the boundaries for some technologies, the Procal 2000 emissions monitoring system has been proven in long term service onboard ships as a robust and reliable method of confirming compliance with maritime emissions regulations.

Materials used in the SCR process

The advanced Procal P2000 analyser is used globally on many industrial SCR systems as it provides an in-situ measurement without the need for high maintenance sample handling systems that are associated with costly extractive systems. Stainless steel sintered panels form part of the P2000 in-situ sample cell and allow the unmodified gas to enter the cell so that analysis of a truly representative gas sample can be achieved. P2000 analysers can be individually configured to a process stream both upstream and downstream of the SCR. Located on the entry to the SCR a P2000 analyser can be configured to measure high NO_x gas concentrations that are usually in the range 0-2500ppm. A P2000 analyser installed at the SCR exit after the catalytic reduction has taken place can be configured to measure a NO_x range of 0-200ppm or lower.

The SCR process consists of injecting ammonia (NH₃) into the boiler flue gas and passing the flue gas through a catalyst bed. The NH₃ is absorbed onto the catalyst and reacts with the NO_x to form diatomic nitrogen (N₂) and water vapour. Several types of reduction agent are available such as anhydrous ammonia, aqueous ammonia or urea. Large Industrial SCR operators prefer the use of pure anhydrous ammonia as it requires no conversion prior to use in the SCR. The drawback is that anhydrous ammonia being extremely toxic is difficult to store. Alternatively, aqueous ammonia, which is safer to store, can be used but this must be hydrolysed beforehand. A second alternative is Urea which requires conversion to ammonia through thermal decomposition but is the safest material to store.

The catalyst is normally a ceramic material in a honeycomb or plate structure that is a mixture of substrate (titanium oxide) and active components (oxides of vanadium and, in some cases, tungsten). The honeycomb form is an extruded ceramic with the catalyst either incorporated throughout the structure (homogeneous) or coated on the substrate. In plate geometry, the support material is generally coated with a catalyst. Plate-type catalysts have lower pressure drops and are less susceptible to plugging and fouling than the honeycomb types, but plate configurations are much larger and more expensive. Honeycomb configurations are smaller than plate types, but have higher pressure drops and tend to plug much more easily.

SCR arrangement

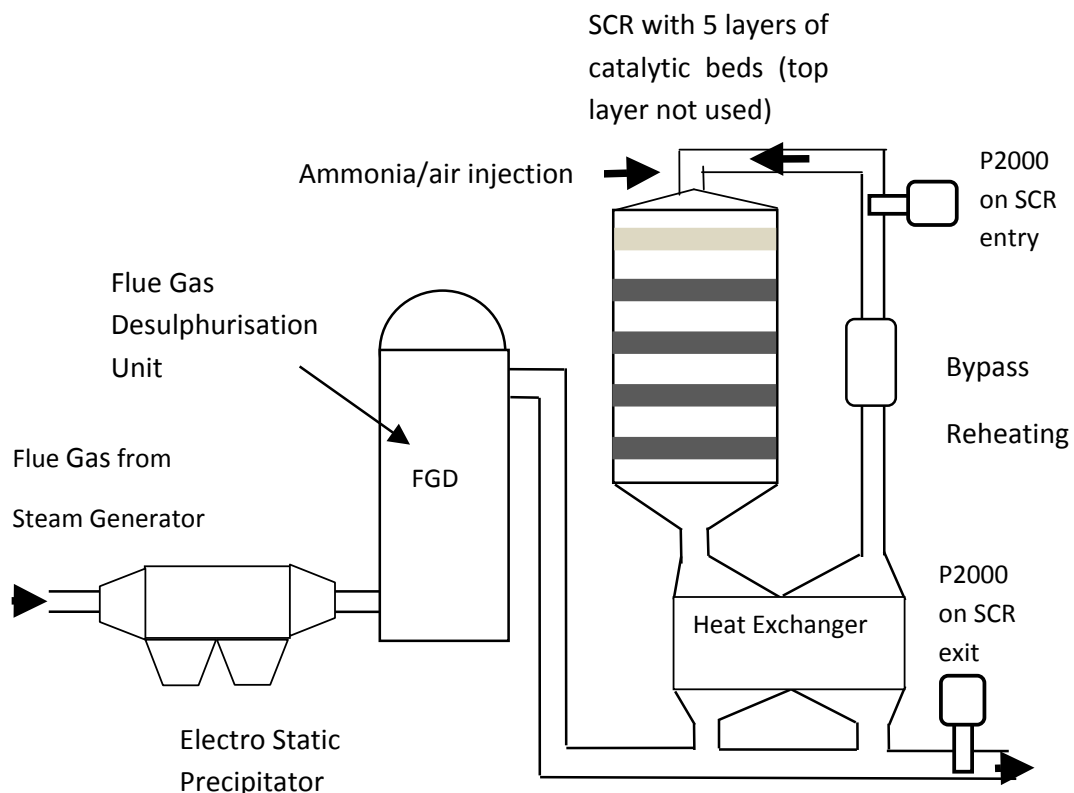
Depending on a utilities requirements (new plant, retrofit, space availability), NO_x reduction can be performed in a variety of configurations.

Tail-end arrangement

A configuration often referred to as a tail-end arrangement is usually employed in European Power stations and incinerators is shown in figure 1. In this configuration, the SCR unit is placed after the precipitator and the flue gas desulphurization (FGD) unit. The flue gas entering the SCR contains very little dust, SO₂ and catalyst poisons as these are removed by the precipitator and FGD units. In figure 1 a P2000 is shown installed on the entry to the SCR and a second P2000 installed on the exit measuring the cleaned DeNO_x flue gas. This system of P2000 analysers not only measures emissions, but also enables the plant operator to monitor and control the required ammonia injection to optimize the efficiency of the SCR.

As the catalyst activity reduces, additional catalyst can be installed in the available spaces in the reactor. As deactivation continues, the catalyst is replaced on a rotating basis, one layer at a time, starting from the top. The disadvantage of the tailend configuration is that preheating of the flue gas prior to the SCR is required which increases installation and operation costs.

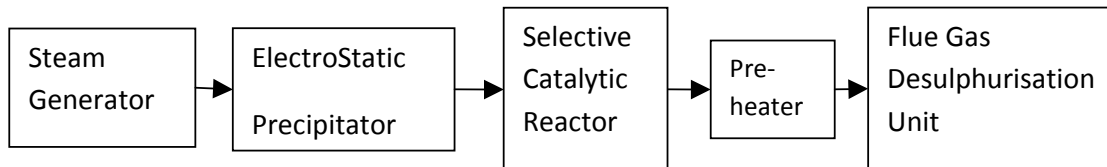
Figure 1 Tailend SCR arrangement



Low Dust Configuration

In this arrangement, the catalyst is situated downstream of a hot-side electrostatic precipitator that is downstream of the boiler as shown in figure 2. In this arrangement the dust is removed from the flue gas before entering the SCR reactor. A high level of SO₂ is still present in the flue gas but the gas temperature is high enough to require no further re-heating. The P2000 analyser allows both NO_x and SO₂ gases to be measured simultaneously. Cross sensitivity between the measurements is minimised as the Infra Red gas absorption is measured by using two specific wavelengths per monitored gas component. The P2000 operation, automatic zeroing and gas calibration checks are “fully challenged” in that all operating modes use the same optical path and system components.

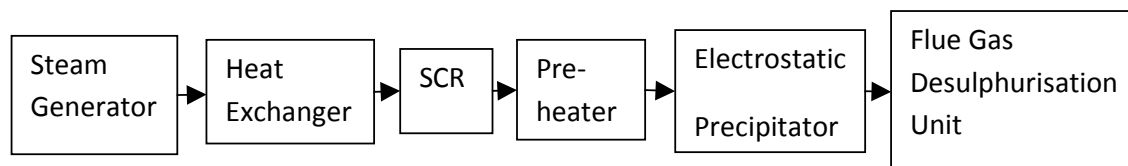
Figure 2 Low dust SCR



High Dust Configuration

In a high dust configuration, the SCR reactor is installed directly downstream of the heat exchanger and upstream of the air pre-heater. The main advantage of this arrangement is that preheating of the flue gas is not necessary. The flue gas temperature normally varies between 300°C and 430°C (570°F and 810°F). The P2000 sits comfortably and can be used at temperatures upto 350°C (662°F). Higher temperatures can be achieved with the Procal in-situ cooler accessory.

Figure 3 High dust SCR



Factors affecting the performance of an SCR

Operating Temperature of SCR

The presence of a catalyst in the reaction between ammonia and nitric oxide which produces nitrogen and water reduces the natural reaction temperature of between 815-1204°C (1500-2200°F) to a more manageable temperature of 250-427°C (400-800°F). The optimum temperature range depends on the type of catalyst used and the flue gas composition. An SCR unit will normally tolerate temperature fluctuations of $\pm 90^{\circ}\text{C}$ ($\pm 200^{\circ}\text{F}$).

To perform correctly tuning of the SCR is required where control of both the uniformity and flow rate of the flue gas is required to optimize the chemical reaction of the NO_x and ammonia gas at the catalytic beds. Without tuning, SCRs can exhibit inefficient NO_x reduction and ammonia slip.

Ammonia Slip

This is the industry term for ammonia gas that passes without reaction through the SCR. Ammonia slip can occur when the ammonia is over injected into the gas stream, the temperature is too low or the catalyst has degraded. The Procal P5000 UV gas analyser can be used to measure emissions of low concentrations of ammonia in the range 0-25ppm and has been used in ammonia slip applications. The ammonia flow injected into the SCR is normally characterised for all process conditions. The control of the ammonia being based on the measurement of NO_x in the flue gas as it enters and leaves the SCR, which can be measured by a set of P2000 analysers as described above.

Plugging and Contamination

The Procal 2000 design includes highly effective sintered filters that prevent the ingress of particulate matter into the sample cell and a heater to prevent condensation and deposits where the exhaust is below its dew point. An in-situ heater with a high pressure blow back feature is also available to remove the build-up of fly ash.

However, plugging and contamination during normal operation or abnormal conditions can badly affect SCR systems. The porous construction of the catalyst material, which provides a large surface area for the catalytic reaction, is subject to plugging. Plugging can result from fine particulates, ammonium salts, silicon compounds and fly ash that binds with the catalyst. Ammonium salts such as ammonium sulphate or ammonium bisulphate can be formed in fuels that have high sulphur content. Plugging can be prevented by the use of soot blowers, cleaning contaminants from the SCR when it is off line or by increasing the temperature of the exhaust gas.

Catalytic poisoning can also be a serious problem as the ability of the SCR to chemically change the NO_x gases into N_2 and H_2O will become ineffective and can also produce higher NO_x readings when ammonia gas is oxidised. Poisonous chemicals include Halogens, Alkaline Metals, Arsenic, Phosphorus, Antimony, Chrome and Copper.

P2000 analyser installation on SCR systems around the world

Michigan City

The Michigan City Generating Station, which is operated by Nipsco in the USA, has two SCR systems supplied by Black & Veatch. Each SCR system has a P2000 installed measuring NO between 0-800ppm and H_2O 0-15%. The P2000s are fitted with in-situ coolers allowing the analysers to operate at the process temperature of 500°C (930°F).



Michigan City Generating System, USA with 2x P2000s

Queensland Australia

Procal has provided 8x P2000s for use on Orica plants in Queensland Australia. Initially, the P2000 was used for continuous emission monitoring but P2000 units are now also used for process efficiency applications including NO_x catalyst reduction unit control. P2000s measure the following gases NO 0–500ppm, NO 0–2,500ppm, NO_2 0–300ppm, NO_2 0–1,500ppm and N_2O 0–500ppm.



Orica Plant Queensland Australia

Ontario Canada

The P2000 was chosen for both CEM and SCR control by Dyno Nobel in Ontario, Canada. Four P2000s measuring NO 0–500ppm, NO₂ 0–500ppm, N₂O 0–500ppm, N₂O 0 – 1%, CH₄ 0 – 8,000ppm and CO₂ 0 – 15%.



A P2000 installation at Dyno Nobel in Ontario, Canada