

Recovery Boiler SCR - A Challenge and an Opportunity in Retrofit Cases

Executive Summary

SCR – Selective Catalytic Reduction is a well-established and widely used technology for NO_x removal from power boiler flue gases. Until now there has not been any need to utilize SCR in recovery boilers. Sufficient 200 mg/m³ (6% O₂, dry gas) is an achievable NO_x emission level with primary means only. There indications from China and some European countries that the target emission level will be 100 mg/m³ (6% O₂, dry gas) in the near future. This is not achievable by air staging or even by SNCR in recovery boilers with normal kraft black liquors having N₂ content of 0.1 % or higher in dry solids.

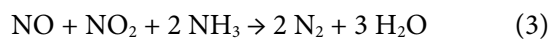
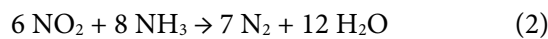
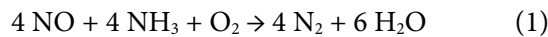
In recovery boiler retrofit cases there are three challenges for SCR: SCR reactor inlet flue gas temperature, probable SO₂ in the flue gas and excess particulate concentration after the electrostatic precipitator. Flue gas temperature should be ~250 °C and SO₂ preferably below 5 mg/m³ to avoid formation of harmful ammonium bisulfate. Dust concentration should stay below 30 mg/m³n after ESP to avoid catalyst blockages. New recovery boilers run with very low SO₂ emissions but some variation and peaks may occur. The desired temperature is achievable with certain high power features. Additional electricity production creates good payback for the high power investments.

In this paper a theoretical study is presented for a retrofit case of a recovery boiler where an SCR is utilized to lower NO_x from 200 to 100 mg/m³ (6% O₂, dry gas). Necessary high power features are implemented to raise the flue gas temperature high enough for the SCR.

Introduction

Selective catalytic reduction (SCR) of NO_x emissions has been in use from the early 1970s. In the U.S.A. alone, over 1,000 SCR systems have been installed in many different industries, including utility and industrial boilers, process heaters, gas turbines, internal combustion engines, chemical plants, and steel mills. SCR is typically used in stationary source combustion units requiring a higher level of NO_x reduction than achievable by selective non-catalytic reduction (SNCR) or primary combustion controls. An SCR system could be designed for highest NO_x removal, in excess of 95 percent (%) efficiency.

The reducing agent used in the majority of SCR systems is gas-phase ammonia (NH₃) because it readily penetrates the catalyst pores. The ammonia, either in anhydrous or aqueous form, is vaporized before injection by a vaporizer. After a series of reactions, the ammonia radicals come into contact with the NO_x and reduce it to N₂ and H₂O. The representation of the governing reaction equations is given here:



The catalyst lowers the required activation energy for the reduction reactions and increases the reaction rate even at reasonably low flue gas temperature. In the catalytic reaction, activated sites on the catalyst rapidly adsorb ammonia and gas-phase NO to form an activated complex. The catalytic reactions result in nitrogen and water, which are then desorbed to the flue gas. The site at which the reaction occurs is then reactivated via oxidation. [1]

If the flue gases contain any SO₂ the undesired parallel reactions of the reactions in equations 1-3 are.



Below the dew point of ammonium bisulfate, ammonia and sulfuric acid condense as liquid ammonium bisulfate, NH₄HSO₄ (ABS), in the catalyst pore structure which reduces the performance. At SCR temperatures, gaseous sulfuric acid is in equilibrium with SO₃ and the ABS dew point therefore depends on water content, ammonia content and SO₃ concentration [1, 2].

Field measurements in running coal fired boilers have shown ABS formation temperatures remaining below 220 °C [4]. In these measurements, the formation temperature decreases down to 160 °C with decreasing SO₂, NO_x, and NH₃ concentrations. A bench-scale experimental simulation of a single-channel air preheater gave somewhat higher numbers, 227 – 247 °C for the formation temperature [5]. In this case, sulfuric acid and/or ammonia concentrations of the gas were high, explaining the higher temperatures.

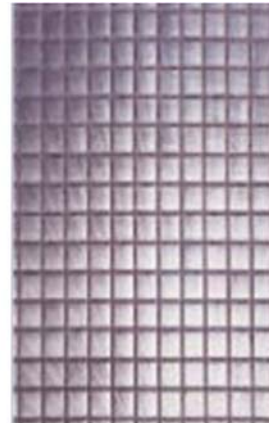
Currently typical catalyst materials are titanium dioxide TiO₂ as a catalyst support, vanadium pentoxide V₅O₅ as principal active component, and tungsten trioxide WO₃ as a promoter. Structure types, plate, honeycomb, and corrugated, of the catalyst units are shown in **Figure 1 (next page)**. [3]

Depending on the application, the SCR reactor can be located either into the high dust or low dust location in the flue gas duct. The different locations are shown in the **Figures 2 and 3**. The high dust location is utilized typically in coal, peat and "clean" biomass boilers. The low dust location is used in forest residue and waste fuel boilers. Obviously the same will be utilized in recovery boilers and lime kilns. In low dust applications, the SCR reactor is located downstream of the particulate and SO₂ capture devices. Heat is recovered after the SCR unit.



Plate

- Rolled
- Coated



Honeycomb

- Extruded
- Coated



Corrugated

- Composite
- Hybrid

Figure 1. Structure types of the catalyst units

In the high dust location, flue gas temperature is typically 240 – 420 °C, and in the low dust location preferably 240 – 250 °C to avoid condensation of possible ammonium bisulfate in the flue gases.

Throughout the years, several authors have pointed out the dangers of sulfuric acid corrosion in black liquor recovery boilers. Sulfuric acid in the flue gas would lead to severe corrosion of components, such as economizers, air preheaters, the flue gas duct, and SCR reactor - if their material temperature is below the sulfuric acid dew point temperature. However, recent research of Kraft recovery boilers has proven that during normal full load operation there is no sulfuric acid in the stack gases of these boilers [6, 7]. Thus, in the case of Kraft recovery boilers, ABS should not be a problem during stable full load operation. This is because modern recovery boilers run with high furnace bottom loads and high black liquor dry solids, basically without any SO₂ in the flue gas. Consequently, the reactions in equations 4-6 do not take place and there is no sulfuric acid H₂SO₄ in the gas to form ammonium bisulfate NH₄HSO₄ with ammonia NH₃. Nevertheless, as long as we do not have SCR running in recovery boiler applications to gain experience, we must consider ABS possible and a challenge.

Despite low ammonium bisulfate production, some deactivation of the catalyst always takes place. Typical SCR catalyst lifetime is about 16,000 – 24,000 hours. Regeneration of the catalyst may expand the life time and thus reduce the operational costs of the SCR. Currently most often the catalyst units have to be removed from the reactor for regeneration. This is

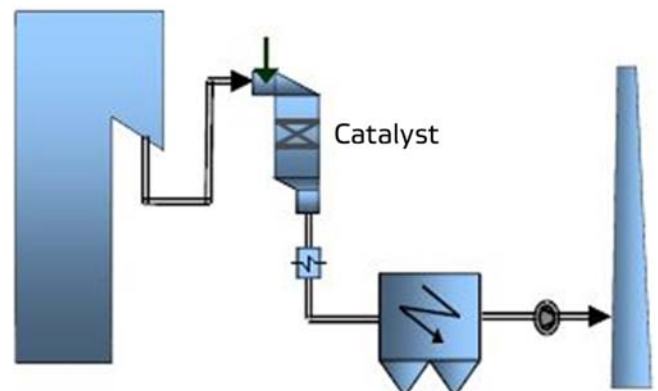


Figure 2. High dust SCR application

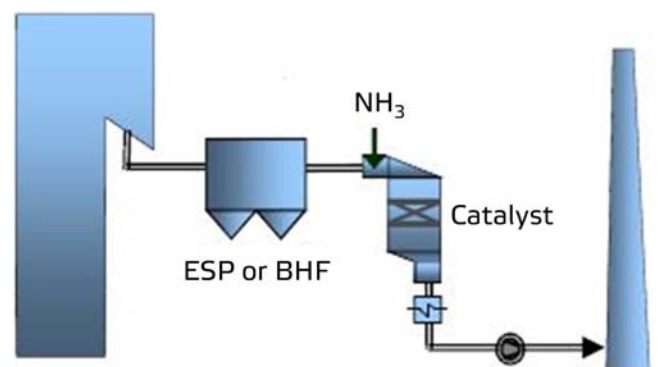


Figure 3. Low dust SCR application

quite laborious and costly. However, there are methods under development and testing which use acidic or alkaline liquids to wash catalyst units inside the reactor. Especially the alkali solution washing might be a promising approach for the regeneration of SCR catalyst [8].

In a retrofit case of the recovery boiler, where SCR is installed after the ESP into the low dust location, modifications need to be done to the heat transfer concept of the boiler to increase the flue gas temperature to the acceptable level. Also, an efficient control system is needed to secure the catalyst from contamination during disturbed boiler operation situations.

A retrofit case recovery boiler

The Kraft recovery boiler selected for this exercise is located in a Scandinavian pulp mill. The capacity of the boiler is 3600 t_{DS}/day. This mill has no need to reduce NO_x emissions - the boiler was selected to represent a modern midsize recovery boiler. This exercise was done as an R&D project to be ready to propose SCR for an existing recovery boiler when needed. The guarantee value of NO_x emission of the boiler is 200 mgNO₂/m³n. A scenario of 100 mgNO₂/m³n in the future was set as a target of the project. Necessary changes into the design of the steam process, flue gas treatment, lay-out, and automation were evaluated. SCR reactors with the ductwork and auxiliaries were designed and added to the lay-out. A major question from the beginning was: what is needed to raise the flue gas temperature at the exit of the electrostatic precipitator from 150 °C to 240 °C? Another important question was: how to control the SCR in situations where too high SO₂ concentrations are generated in the recovery boiler?

High power concept

Several high power concepts were generated for comparison of process operation and economy. After thorough calculations, the concept shown in **Figure 4** appeared to be the most economical in this case. In this concept the flue gas temperature is raised to 230 – 240 °C by two consecutive feedwater heaters. Temperature can be controlled to a sufficiently high value even on partial loads of the boiler. MP2 and MP extraction steams are used as a heating medium. In this temperature flue gases are fed into the electrostatic precipitators and SCR reactors. Flue gases are cooled down to 130 °C by a gas to water flue gas cooler. Cooling water serves heat to demi water and to combustion air using a set of additional heat transfers units.

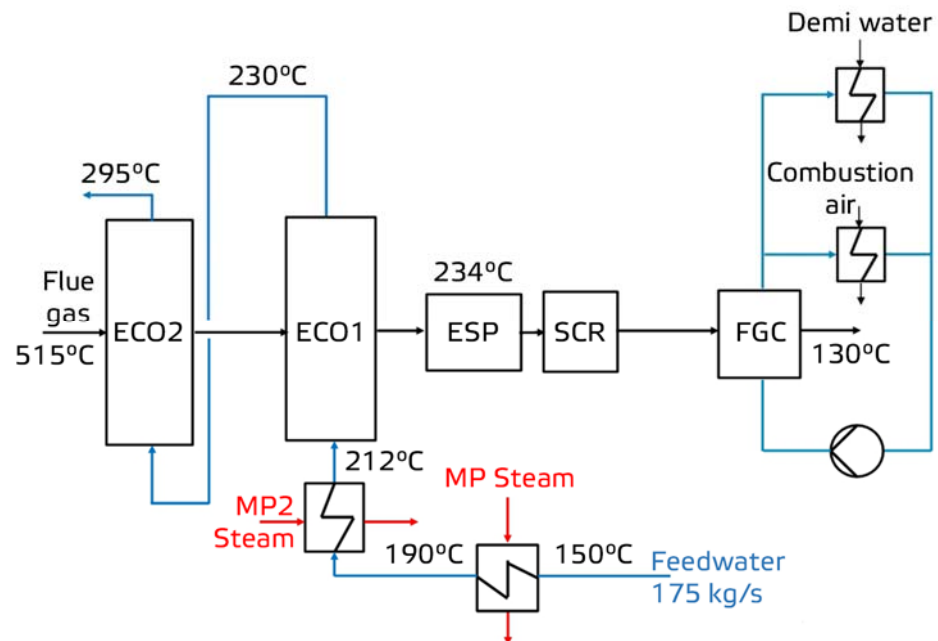


Figure 4. High power concept in a retrofit SCR installation

By this connection more than 13 MW extra electricity is produced by the recovery boiler, having a condensing tail steam turbine. This represents about 14 % of increase in electricity production. Steam

generation is increased roughly by 5 %. An additional superheater is needed to maintain high enough attemperation and the steam temperature at original 505 °C temperature also with fouled superheaters and on partial loads.

The space for another super heater was reserved from the beginning as shown in **Figure 5**. If there was no space readily available for an additional superheater, some other concept for raising the flue gas temperature and extra power production could be more economical.

Installation

Originally there are three flue gas lines with the electrostatic precipitator in the recovery boiler of this study as shown in **Figure 6**. The total flue gas amount, split to three ESPs, is 190 m³/n/s. When the temperature is raised to 240 °C, the actual flue gas flow rate is increased by 12 %. One additional flue gas line with a new ESP is needed to maintain low enough actual flow rate and to lower the flue gas particulates concentration to the required < 30 mg/m³n. A new lay-out with one additional ESP and four SCR reactors is shown in **Figure 7**. Four SCR reactors are located on the clean side of the electrostatic precipitators, above the existing ID fans and ductwork in order to minimize the shutdown time needed for installation.

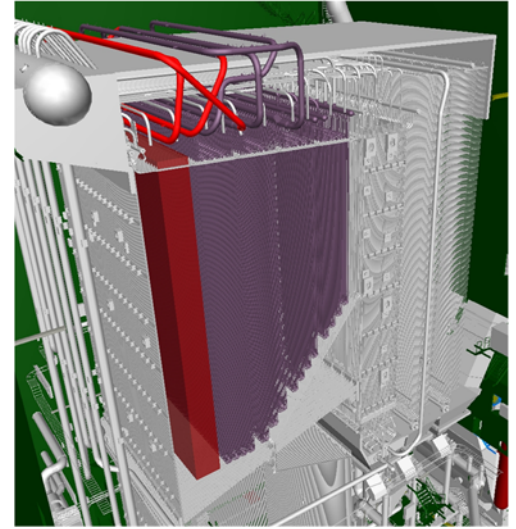


Figure 5. An additional super heater is located in a reserved open space.

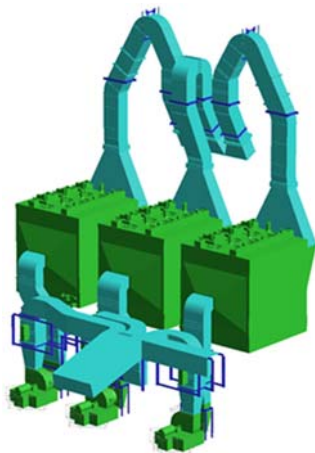


Figure 6. Original flue gas ductwork and electrostatic precipitators

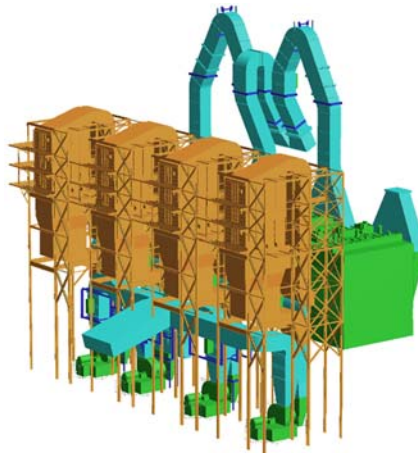


Figure 7. New layout of the flue gas ductwork, electrostatic precipitators and SCR reactors

Changes to the recovery boiler and installation of the SCR system require two installation shutdowns of the recovery boiler. Twelve days are needed for installation of the additional secondary superheater and for making other boiler changes. Also, connections of the fourth flue gas line and the SCR reactor are done during this shutdown. Five additional days are needed for connecting the three other flue gas lines and SCR reactors which were preassembled and erected while the boiler was running. The catalyst is loaded into the reactors during this shutdown.

A closer view of the SCR reactor is shown in **Figure 8**.

Each reactor has catalyst in two layers and an open space to add one more layer if needed. The flue gas cooler is located at the bottom of the reactors. Each reactor has three sootblowers per catalyst layer using air to clean the catalysts from flue gas dust. Vaporized NH_3 water is injected into the raising flue gas duct before the reactor. The reactor can be isolated from the flue gas duct if necessary by using tight dampers and a bypass duct. Such a situation could be caused by too low temperature or too high dust or SO_2 concentration of the flue gas. The first reaction of controls to these situations would of course be shutting down the ammonia injection. Rapid information about temperature, particulates, and SO_2 are needed for controls.

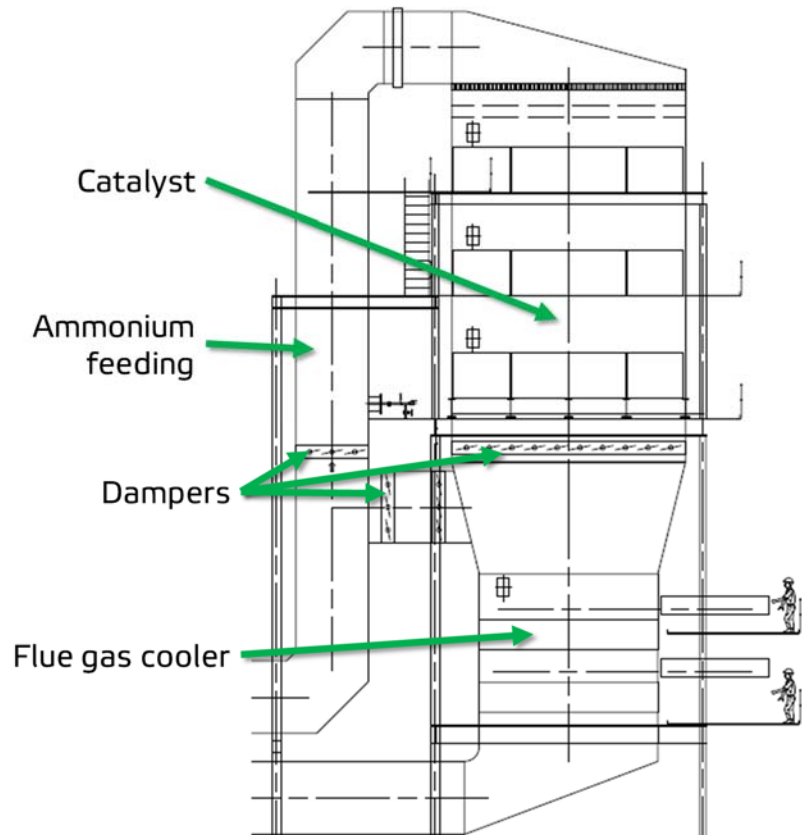


Figure 8. Side view of SCR reactor

Economy

In this study the total investment was estimated, including project execution, SCR with ducting and an additional ESP, recovery boiler modification and mechanical erection. High power modification of the recovery boiler represented a 36% share of the total investment.

A simple payback calculation for the high power modification of the recovery boiler was done. The estimation showed that the high power modification investment pays back in 1.7 years under a prevailing electricity price of 30 €/MWh and with 8500 operational hours. If the total investment was to be paid back by sold extra electricity, the payback time would naturally be higher, 4.7 years.

Conclusions

In this paper a theoretical study was presented for a retrofit case of a recovery boiler where an SCR is utilized to lower NO_x from 200 to 100 mg/m^3 (6% O_2 , dry gas). Necessary high power features are implemented to raise the flue gas temperature high enough for the SCR.

A high power concept with two feedwater preheaters, a flue gas cooler, added stages of air preheaters, and a demi water heater was developed to increase power production and to achieve the target flue gas inlet temperature for the SCR.

With two feed water preheaters, the flue gas temperature can be controlled to the acceptable level even on partial loads of the boiler. An additional superheater was needed to maintain attemperation and the steam temperature.

A fourth ESP with flue gas ducting was added to the boiler because of the higher flue gas temperature. Each flue gas line was furnished with an SCR reactor. Under situations of too low temperature or too high dust or SO₂ concentration of the flue gas, the reactor can be isolated from the flue gas duct by a bypass duct. The first reaction of controls to these situations would be shutting down the ammonia injection. Rapid information about temperature, particulates and SO₂ are needed for controls.

A 14 % increase in electricity production, being 13 MW, was achieved with the used high power concept. With this extra electricity, the investment in high power was estimated to be paid back in 1.7 years. The total investment was paid back in 4.7 years by additional revenue from the extra electricity.

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