VTT Technical Research Centre of Finland

Boiler tube corrosion caused by urea injection of SNCR system

Ekholm, Katri; Tuurna, Satu; Yli-Olli, Sanni

Published in:
Baltica XI

Published: 01/01/2019

Document Version
Publisher's final version

Please cite the original version:
Ekholm, K., Tuurna, S., & Yli-Olli, S. (2019). Boiler tube corrosion caused by urea injection of SNCR system. In *Baltica XI: International Conference on Life Management and Maintenance for Power Plants* VTT Technical Research Centre of Finland.

Boiler tube corrosion caused by urea injection of SNCR system

Katri Ekholm[1], Satu Tuurna[2], Sanni Yli-Olli[2]

[1]Helen Ltd
Helsinki, Finland

[2]VTT Technical Research Centre of Finland
Espoo, Finland

Abstract

This paper aims to describe and discuss two observed cases of boiler tube failures in a combined heat and power (CHP) plant operating in a downtown area of the city of Helsinki. Both cases, first in the steam generator and then in the superheater region, involved a boiler area of urea injection for selective non-catalytic reduction (SNCR) of NOx in the flue gas.

The investigations of the failed tubes showed consistent indications of corrosion caused by prolonged contact of the tube surfaces to liquid droplets of the urea solution, resulting in characteristic corrosion with high rates of wall loss. For improved performance, injection of the urea solution needs an optimal balance in the droplet size so that it is sufficiently large to retain the required reaction time for NOx conversion and small enough to avoid corrosive contact.to the tube walls. The discussion also extends to the available options for NOx reduction in an urban environment.

1. Introduction

Helen Ltd has two boilers firing hard coal and wood pellets in the Hanasaari combined heat and power (CHP) plant in Helsinki. To reduce nitrogen oxide (NOx) emissions, this plant makes use of a selective non-catalytic reduction (SNCR) system.

During combustion, NOx emissions can form by three possible mechanisms: by oxidation of fuel-bound nitrogen compounds (fuel NOx), by oxidation of atmospheric nitrogen present in the combustion air (thermal NOx), or by a series of reactions between hydrocarbons originating from rich flame and nitrogen (prompt NOx). The prompt NOx contribution to total NOx is typically small. However, the expected importance of the prompt NOx will increase, when aiming to NOx reduction e.g. through modified burner design and furnace geometry [1].

SNCR is a cost-efficient solution for NOx reduction, as SNCR does not need a catalyst like selective catalytic reduction (SCR) system. An SNCR system will use a reagent, such a urea or ammonia, injected into the furnace. In urban areas, urea ($CO(NH_2)_2$) is often used as a reagent, because it is safe to store and transport in such environments.

The reaction of NOx reduction is temperature dependent, and the reagent ideally injected into an optimal temperature zone for efficient conversion. In practice, the injection of an aqueous urea solution takes place in the boiler region where the flue gas temperature is close to 1000 °C.

In flue gas, water initially evaporates from the droplet of urea solution, and urea transforms into ammonia (NH_3). The ideal urea-to-ammonia-reaction is as follows.

Urease reaction: urea to ammonia hydrolysis

$$CO(NH_2)_2 + H_2O \rightarrow 2NH_3 + CO_2 \tag{1}$$

The transformation is not always perfect, as it may occur stepwise and produce compounds like ammonium carbamate [1], isocyanic acid (HNCO) [3] and isocyanate (NCO) [4]. The transformation mechanism of urea to ammonia depends on temperature and composition of flue gas, but a typical step is urea decomposition via isocyanic acid [3]:

$$CO(NH_2)_2 \rightarrow HNCO + NH_3 \tag{2}$$

$$HNCO + H_2O \rightarrow NH_3 + CO_2 \tag{3}$$

The formed ammonia reacts with NOx in flue gas:

$$6NO + 4NH_3 \rightarrow 5N_2 + 6H_2O \tag{4}$$

The complete net reaction for NOx reduction with urea is producing nitrogen, water and carbon dioxide:

$$6NO + 2CO(NH_2)_2 \rightarrow 5N_2 + 4H_2O + 2CO_2 \tag{5}$$

The optimal range of reaction temperature is 850-1100 °C, Figure 1. At lower temperatures, the reaction of ammonia is not perfect and an ammonia slip may occur. At temperatures higher than 1100 °C, ammonia may react with oxygen, increasing NOx content in flue gas. The effective temperature window for NOx removal can widen with increasing residence time. Longer residence time at the optimal temperature range promotes reduction reactions even when the dosage of reagent is not optimal. [5–7]

The urea is injected to a boiler as an atomised fog. For maximum NOx reduction, the droplet size should be large enough for sufficient reaction time with flue gas before evaporation. However, too large droplets may not stay in the flue gas but hit the boiler tube surfaces before evaporation, promoting corrosion and wall thinning [8,9]. Control of wall thinning and corrosion will require proper material selection, design and positioning of injection ports, and optimised energy to atomise reagent into appropriate range of droplet sizes.

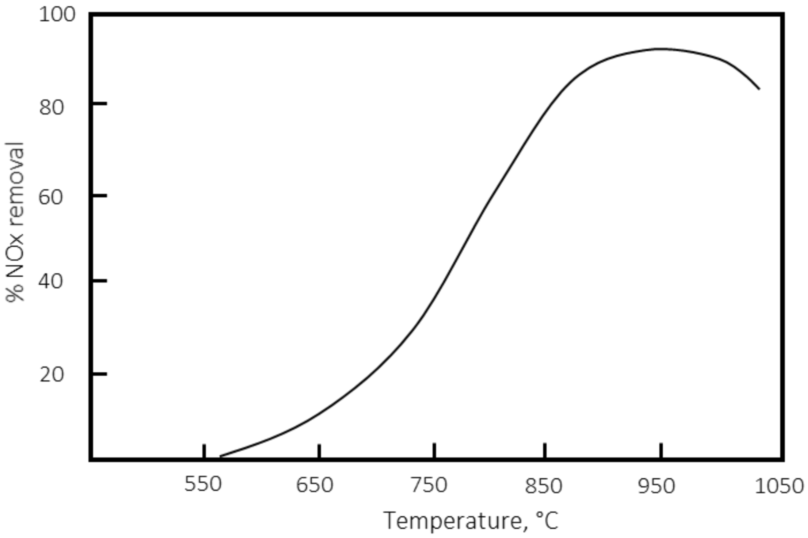

Figure 1. Typical SNCR temperature window according to the SNCR Committee [5].

2. Failure cases

The operating company Helen Ltd is using urea for NOx control, because urea is safe to transport and store for the Hanasaari power plant, located in downtown Helsinki. The plant includes two nearly identical boilers, with combustion and urea injection arrangement shown in Figure 2.

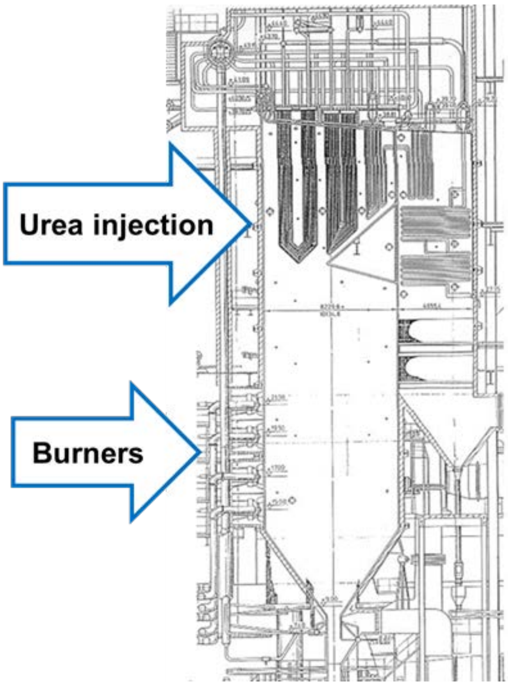

Figure 2. Arrangement of urea injection in Hanasaari boilers.

The SNCR systems are in principle similar in both boilers, with differing nozzle types. One of the boilers has a self-made injection system with thin nozzles 20 cm inside the furnace, and thin pipes working as nozzle holders, welded outside the boiler.

The other boiler has vertically adjustable commercial lances, Figure 3.

Figure 3. Commercial urea injection lances on the boiler front wall; secondary superheater on the right.

In Hanasaari power plant the flue gas temperature is optimal for urea injection at the level of secondary superheater, with flue gas temperature of about 1100 °C and water temperature of 350 °C in boiler tubes at that level. The urea injection nozzles are located on the front wall at three levels in the boiler.

Urea is injected into the boiler as 2.5 to 5 percent aqueous solution at a temperature of 20–25 °C. As a 40% aqueous solution, the pH value of urea is 9.60. The injected urea contains some calcium, iron, copper, zinc, chromium, nickel, aluminium, magnesium, sodium, potassium and lithium. Chemical analysis of the urea solution has also indicated some chlorides, sulphates and thiosulphates.

2.1 Case 1: boiler tube failure with initial injection nozzles

In March 2016, two leaking boiler tubes were found associated with an initial construction of urea injection nozzles. Steam was flowing into the boiler room from the holders of the urea injection nozzles. In this boiler, the injection nozzle holders are small tubes, welded between two boiler tubes and extending through the boiler wall. The holes for the urea injection nozzles were made already in 2013. However, they were not in use before 11 days prior to the observed leakage.

After entering the boiler, indications of corrosion were found near the holes for installing the urea injection nozzles.

Figure 4. Corroded holes for injection nozzles inside the boiler.

The visual and microscopic inspections indicated that the leakage was due to corrosion that started from a gap between the boiler tube and a small diameter tube installed for the urea injection nozzle. Boiler tube material is 15Mo3 steel.

Figure 5. A section of a failed boiler tube.

Sectioning of the corroded boiler tube showed corrosion on the fireside and at the connecting point of the boiler tube and the injection nozzle holder. After cutting down the part into smaller pieces severe corrosion was found also inside the crevice between boiler tube and injection nozzle holder. Leaking holes were found on the fireside of the tube and inside the crevice (varied in different tubes).

Figure 6. A corroded tube sectioned for microscopic examination; fireside on left, place for injection nozzle on top.

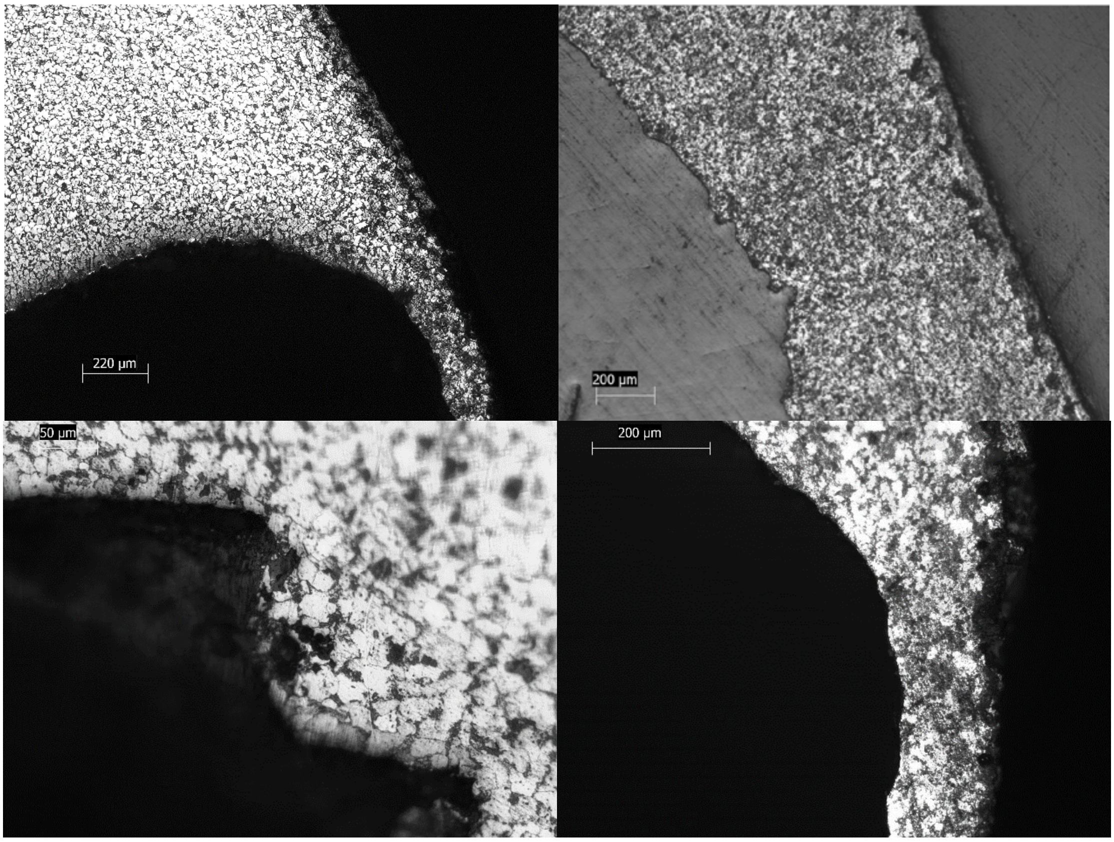

Figure 7. Fireside corrosion on the affected boiler tube.

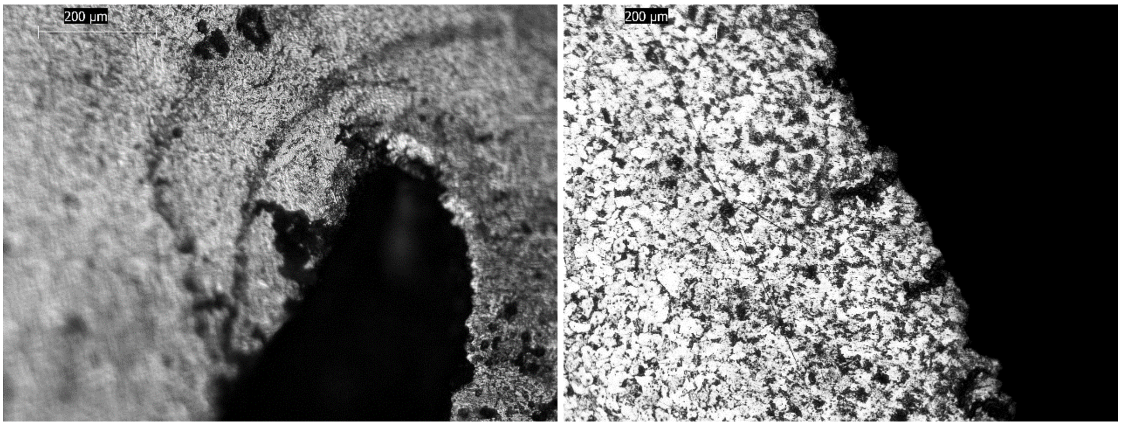

Figure 8. Corrosion in the crevice.

The microstructure of the base material was consistent with that expected of the steel grade 15Mo3. Microscopic examination showed transgranular corrosion, with corrosion pits in the crevice.

Besides crevice corrosion, the corroded fireside area of the boiler tube showed pits and aggressive local corrosion.

EDX analysis indicated large amounts of sulphur in the deposits [10].

2.2 Case 2: Superheater tube failures

In summer 2017 before the scheduled annual maintenance outage, a leakage occurred in the secondary superheater made of X20CrMoV12-1 steel. Two superheater tube screens included in total nine failed tubes, with leakage location at the level of the urea nozzles.

Macroscopic examination showed corrosion markings corresponding to the boiler (steam generator) tube leakage of the previous year. Figure 9 shows a failed superheater tube, assumed to indicate initial (primary) corrosion damage. Similar primary corrosion markings appeared in five failed superheater tubes, and the resulting steam flow had damaged four additional tubes, causing them to fail as well.

Figure 9. Failed superheater tube with indications of primary corrosion damage [11].

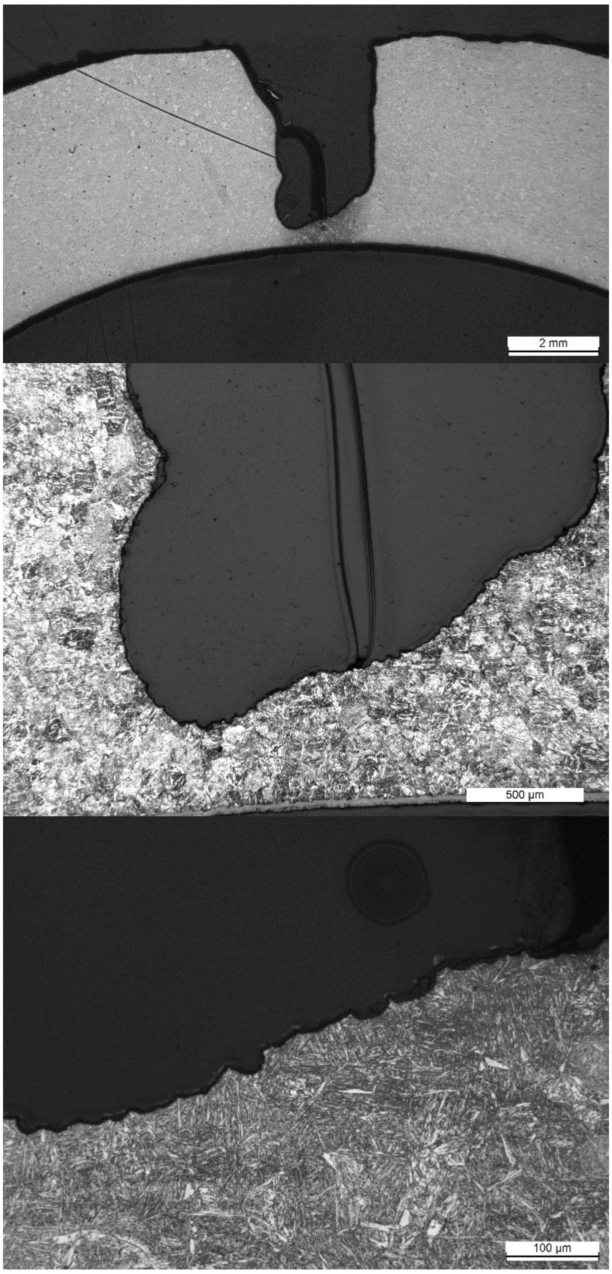

Figure 10. Cross-section of a failed superheater tube, indicating external corrosion [11].

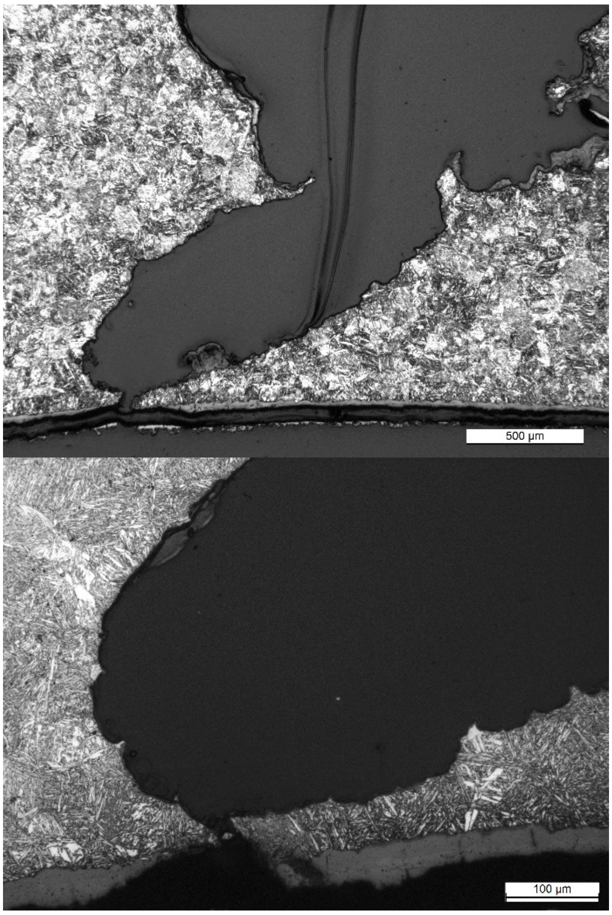

Figure 11. As in Fig. 10, adjacent cross-section [11].

The samples had a martensitic microstructure consistent with that expected of the steel grade X20CrMoV12-1. Microscopic analysis confirmed that the primary failure was due to aggressive external corrosion.

Failed tubes and surface deposits were examined with SEM/EDS and XRD analysis. Calcium sulphate ($Ca(SO_4)$), iron oxides (Fe_3O_4 and Fe_2O_3), silica (SiO_x) and ammonium nitrate (NH_4NO_3) were found in the surface deposits [8]. Parts of the deposits also indicated high contents of sulphur [8]. At this level, there had been an experiment of urea injection with pressure, instead of pressurized air like in the other nozzles.

2.3 Case 3 : Boiler tube failure at commercial injection lances

The other boiler in Hanasaari has commercial urea injection lances. In the annual maintenance in summer 2017, areas below the urea lances showed aggressive corrosion, Figure 12. Visual inspection indicated appearance that resembled the corrosion near the urea injection in the other boiler. No tube leakage was noticed before shutdown and entering the boiler. This case required no microscopic examination.

Figure 12. Corrosion below the urea injection lances.

3. Discussion

All three failures occurred within the area of urea injection. When the first boiler tube failure occurred, it was not certain if urea had caused the corrosion. The presence of ammonium nitrate on the surface of failed superheater shows the traces of urea droplets on the corroded area. Corrosion marks were similar to the corrosion next to urea injection nozzles.

Corrosion may occur if a liquid urea droplet hits a hot steel surface.

The corrosion caused by urea injection must have been fast and aggressive. The corrosion has been local and resembled worm-paths. Urea injection was started less than two weeks before the first failure occurred and the superheater failure happened not long time after new type of injection nozzles were assembled on the front wall.

The actual cause of the corrosion is not completely understood. Urea may transform into ammonia in different stages. Elements in flue gas, like sulphur, might also have an effect to accelerate corrosion. In Hanasaari, large amount of sulphur was found in the deposits.

Corrosion occurred in carbon steel as well as in martensitic stainless steel.

For maximum NOx reduction, urea droplets should be rather large. Too big a droplet may hit the tube surface, causing aggressive corrosion. With urea injection nozzles, the actual size of injected drops is not well defined. However, the investigation of the urea nozzles showed that some of the used nozzles produced drops that were larger than intended. These large droplets have fallen below the urea injection nozzles to the boiler tubes, causing corrosion of tube surfaces. The droplet does not evaporate if it remains in contact with the injection nozzle that is cooled by urea solution inside the nozzle.

Injecting urea solution is known to cause more corrosion than injecting ammonia [12]. To eliminate corrosion, injecting ammonia would be a possible solution [13]. The NOx reduction reaction starts when water has evaporated and urea converted to ammonia. By injecting aqueous ammonia solution instead of urea solution, the reaction time would decrease. Shorter reaction time will reduce the probability that a corrosive droplet will contact a tube surface.

Because of the challenges related to transportation and storage of ammonia in downtown Helsinki, such a use of ammonia is not an option. However, another approach could be urea conversion into ammonia with a hydrolyser.

The construction of the self-made injection nozzle system enabled crevice corrosion. In the annual maintenance outage in summer 2016, the construction of the urea injection hole was changed and holes were coated with HVOF-coating, which have chromium carbides in nickel matrix. The urea injection was continued.

Examination showed that some of commercial urea lances were not working properly and they were leaking large droplets.

Studying these failures caused by urea injection have taught to be careful with urea nozzles. The risk of tube failure is significant if drops entering the flue gas are too big or the urea injection is not working properly.

The applied coating has protected pipes. Areas near urea nozzles are inspected in every annual maintenance. The condition of the nozzles is monitored and new experiments are made with extra care.

If urea is used as a reagent in the design and placement of injection nozzles need to be done with care.

After fixing the cause of these failures and protected exposed tubes with coating, new failures have not occurred. The last failure was ~two years ago.

4. Conclusions

The paper describes and discusses three observed cases of boiler tube failures in a CHP plant operating in the city of Helsinki. The cases on wall and superheater tubes involved a boiler area of urea injection for selective non-catalytic reduction (SNCR) of NOx in the flue gas. The failure investigations showed consistent indications of corrosion caused by prolonged contact of the tube surfaces to liquid droplets of the urea solution, resulting in characteristic corrosion markings and high rates of wall loss. For improved performance, injection of the urea solution needs a balanced droplet size that is sufficiently large to retain the required reaction time for NOx conversion and small enough to avoid corrosive contact to the tube walls. Options for combustion with NOx reduction in an urban environment are also addressed in brief.

References

1. J.J.W. Yuan, Prediction of NOx Emissions in Recovery Boilers – An Introduction to NOx Module, 1999, 14 p.
2. Q.A. Acton, Nitrogen Compounds - Advances in Research and Application, Atlanta: Scholarly Editions, 2013.
3. O. Finnerman, Modeling and simulation of a turbulent spray urea-SNCR for biomass exhaust gas aftertreatment, Gothenburg: Chalmers University of Technology, 2015.
4. H. Chen, L. Hong, L. Chen, D. Chen, L. Yin and S. Huang, Reaction Characteristics of SNCR De-Nox in Moderate Temperature Range with Urea Spiked Hydrazine as Reducing Agents*,* 2013.
5. White Paper Selective Non-Catalytic Reduction (SNCR) for Controlling NOx Emissions, SNCR Committee, Institute of Clean Air Companies, Inc. 2008
6. C. Locci,·L. Vervisch, B. Farcy,·P. Domingo and·N. Perret. Selective Non-catalytic Reduction (SNCR) of NitrogenOxide Emissions: A Perspective from Numerical Modeling, Flow Turbulence Combust 2017
7. Z. Xiaoman, Z. Rongtian and L. Xiaochun, “Research on SNCR Technology in the Denitration Engineering,” *Informatics and Management Science I,* no. 180, pp. 197-202, 2012.
8. W. David L, “SNCR System - Design, Installation and operation Experience,” Doe Netl, Pittsburg, 2002.
9. B. von der Heide, “SNCR Process for Coal fired Boiler, Experiences and Potential for the Future,” Mehldau & Steinfath Umwelttechnik GmbH, Essen, 2010.
10. S. Yli-Olli, “Asiakasraportti: Hanasaaren K3:n ureasuuttimien korroosion analysointi,” VTT, Espoo, 2016.
11. P. Auerkari, S. Yli-Olli and M. Marja-aho, “Asiakasraportti: HaB K3 Sekundaaritulistimen vuoto,” VTT, Espoo, 2017.
12. “Reducing NOx with SNCR and SCR systems using ammonia solution,” Yara, [Online]. Available at: https://www.yara.com/chemical-and-environmental-solutions/exhaust-gas-treatment-for-industrial-plants/ammonia-solution/. [Accessed 28 1 2019].
13. “The SNCR option for large coal boilers,” *Power Engineering International,* vol. 21, no. 2, 1 2 2013.