# Selective catalytic reduction for $NO_x$ abatement: a review of the technology and modeling approaches

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# Stationary sources emission

- The emission of gasses from stationary sources, among which are $NO_x$ (nitrogen oxides), is identified as the one of major sources contributing to environmental pollution, and as such is identified and regulated globally through strict national and international legislatives mandating allowed emission levels from individual sources, all in effort to alleviate some of the environmental concerns and reduce the impact.
- European Union and the member states are obliged to follow the emission standards given in the Directive 2010/75/EU

# Stationary sources emission

- Newly built boilers should abide with the 85 mg/Nm$_3$ $NO_x$ emission limit.
- Older powerplant boilers have less stringent, but still strict emission limits.
- Both newly built and old usually need SCR to abide with regulations and emission standards, often combined with other measures to provide emissions within limits. The most efficient use of SCR is combined with – primary measures, to provide as much initial reduction and prevention of $NO_x$ formation during the combustion process, and hybrid systems with SNCR that would reduce $NO_x$ concentration prior to entering the SCR reactor.

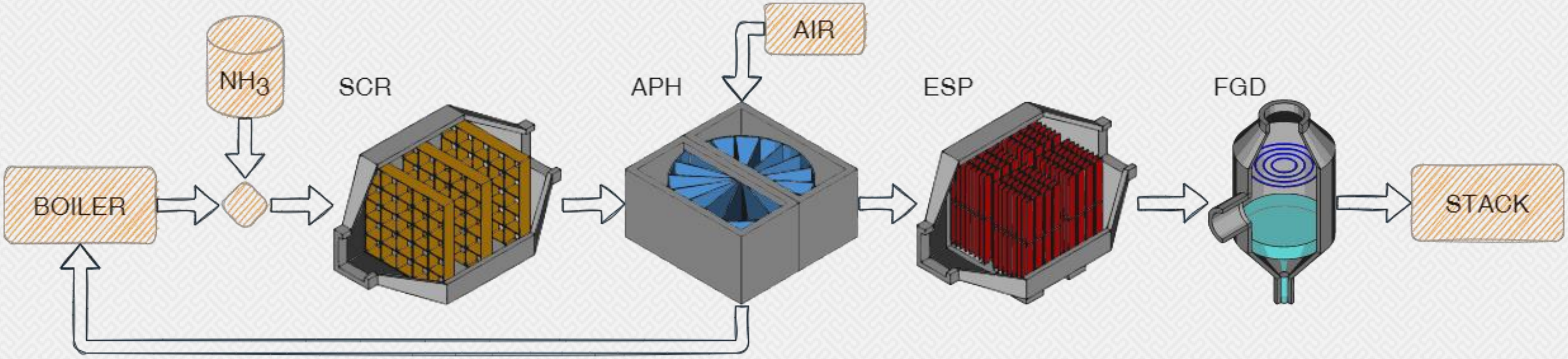
# $NO_x$ emission control technologies

- Primary measures (an effort to slow down formation of $NO_x$ through the modifications to the combustion process)
  - Air staging
  - OFA
  - Low$NO_x$ burners
  - Reburning and flue gas recirculation
- Secondary measures (technologies intended to remove already formed $NO_x$ from the flue gas)
  - SNCR
  - SCR
- Other experimental technologies not commonly used (both primary and secondary measures in experimental or early rollout phases, with some level of promise for application on larger scale)

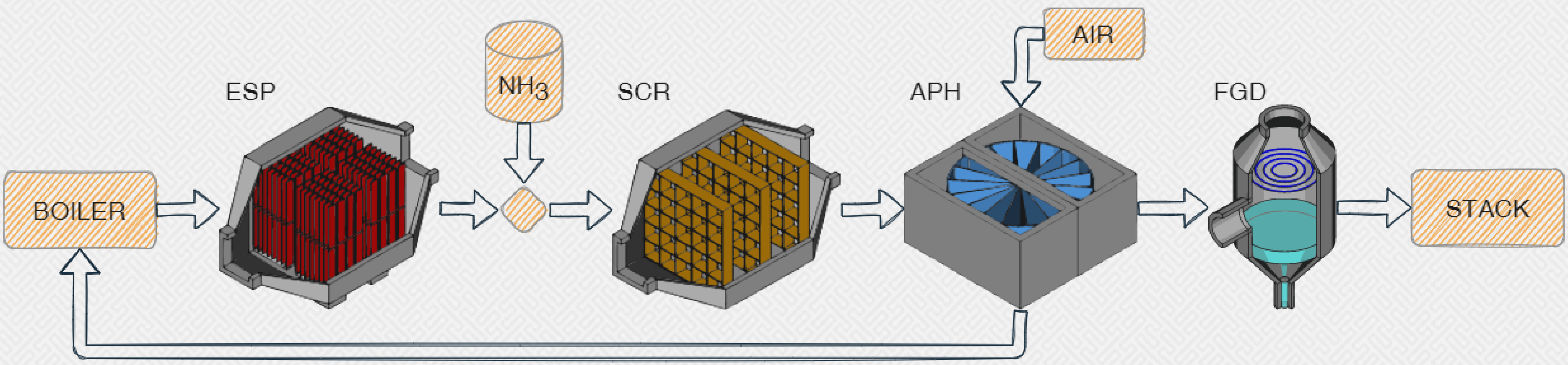
# SCR configurations

- Considering the placement of SCR reactor, three major configurations can be distinguished:
- High dust
- Low dust
- Tail end

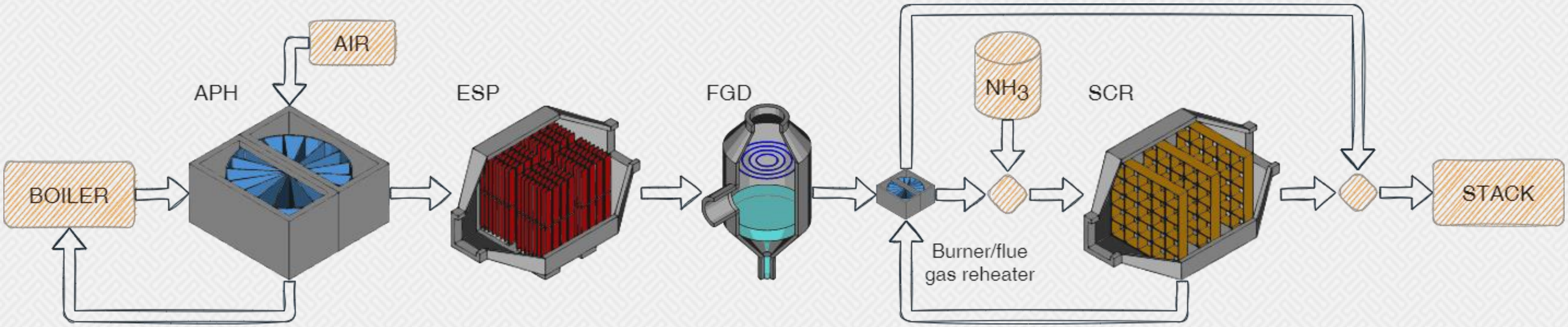
# The high dust configuration



# The low dust configuration



# The tail end configuration



# Catalysts commonly in use

- Depending on working conditions a proper selection of catalyst should be made.
- When selecting the catalyst following parameters play major role:
  - Temperature range, as the different catalysts have different selectivity and performance.
  - Gas species concentration, as the presence of certain species in flue gas may lead to premature loss of catalyst performance, with or without the possibility for full or partial regeneration
  - Presence of particulate matter, which may both react with catalyst, or cause mechanical plugging, or abrasion, leading to necessity for catalyst honeycomb or plates (most common support structure shapes used on powerplant boilers) cleaning or replacement.

# Catalysts commonly in use

- The $V_2O_5$-$WO_3$/$TiO_2$ is most commonly used to treat flue gas from large scale boilers. This catalyst is well suited for the high and low dust configurations, as the local temperatures are around the 300°C in these sections.
- Mn-based catalysts are more suitable for tail end configuration, with lower gas temperatures, but one must also mind the smoke stack minimal temperatures. Some of the catalysts used there are $MnO_x$ which can operate in temperatures range 75 – 175°C, while the Mn-Ce-$O_x$ is more suitable in the range 100-150°C.
- Different authors experiment with other catalysts and preparation methods, and depending on the manufacturers and manufacturing process many others can be found.

# CHEMISTRY BEHIND THE $NO_x$ REMOVAL FROM FLUE GAS

- Expected catalytic chemical reactions
  - The group of reactions used to describe catalytic conversion of NO to $N_2$. Assumed reaction models usually consist of single or two reactions (depending on the amount of NO and $NO_2$ species inside the flue gas). Some authors add third reaction related to NO and $NO_2$ conversion to $N_2$ without the presence of oxygen. Or even the reaction to track undesirable formation of $N_2O$ which can form over certain temperature ranges, depending on the catalyst.
- Undesirable side reactions
  - The unselective behavior of catalyst can contribute to formation of $N_2O$ in the presence of $NH_3$, if the molar ratio of NO and $NH_3$ is lower than 1.
- Non-selective ammonia oxidation
  - In certain catalysts the non-selective ammonia oxidation may occur over the non-selective sites, the intensity of the reaction strongly depend on the catalyst used, and the local temperatures. This phenomenon must be considered when determining the $NH_3$ amount required for the reaction, as it may create imbalance in the NO/$NH_3$ ratio, and cause further problems (underperforming SCR process, formation of $N_2O$, which is green house gas).
- SNCR reactions will occur at significant rates in configurations where the $NH_3$ is injected at higher temperatures, and will contribute to overall efficiency of the process, thus hybrid SNCR-SCR systems are often considered.

# Models commonly used to simulate SCR reactors

- **Porous medium model**
  - This model was used by Liu et al. to simulate the flow through honeycomb structure of SCR catalyst and rectangular flow rectifiers.
  - This model would be well suited to simulate bed SCR reactors, as it replaces the complex internal structure.
- **Source-in-cell model**
  - Represents all catalytic surfaces present in the current fluid cell as the single source.
  - This model provides good amount of information to model the SCR reactions in any geometry, while remaining relatively light on computation side.
- **Global kinetic model**
  - Focuses on the investigation of internal catalyst structure, with corresponding reactions and local species concentration, in order to output data about their macroscopic effects.
  - Can be computation heavy, and lead to long simulation times
- **Density functional theory studies**
  - Some authors use the density functional theory to study the reaction mechanism of catalytic denitrification.
  - This is versatile approach that is popular in computational chemistry. It is the quantum mechanical modelling method.

# Conclusion

- Emission standards and regulations demand the reduction of pollutant gasses emission, and to accommodate these demands measures to reduce $NO_x$ should be applied at both newly built and old boilers.
- Power plant boilers can use several SCR configurations – high dust, low dust, and tail end. Based on the boiler design one of these configurations will be present on the plant.
- Depending on the SCR configuration a catalyst should be selected with such properties to withstand long term use, the choice of catalyst is complex problem, as it depends on both chemical (reaction rates, reactivity with different species in flue gas) and physical properties (pores plugging, mechanical dust/ash deposition).
- Power plants with SCR operating in high or low dust configuration most often use $V_2O_5$-$WO_3$/$TiO_2$, but this may change with discovery/availability of better and more economical catalysts. Honeycomb is usually designed with straight catalyst plated square tubes, or flat plates.

# Conclusion

- Depending on the species present in flue gas several different models for chemical reactions are available, with most authors agreeing on governing equations for the reaction. As the amount of $NO_2$ species in power plant flue gas is relatively low compared to NO, it may be safe to use single reaction for SCR rate, describing the NO reduction, and modelling all $NO_x$ as NO.
- Undesirable side reactions, such as the formation of $N_2O$ should be analyzed, and measures should be undertaken to prevent conditions that would lead to increased $N_2O$ formation.
- Nonselective ammonia oxidation, should be also estimated and used to predict needed $NH_3$ injection to provide best $NO/NH_3$ molar ratio for the SCR.
- From the aspect of numerical modelling, the most promising model is the Source-in-cell model, as it provides ability to simulate more complex geometries with sufficient information about the surface reactions.

# Thank You for your attention