2nd Oxyfuel Combustion Conference

LICONOX – Linde's new technology for removal of NOx and SOx integrated in the CO_2 processing unit

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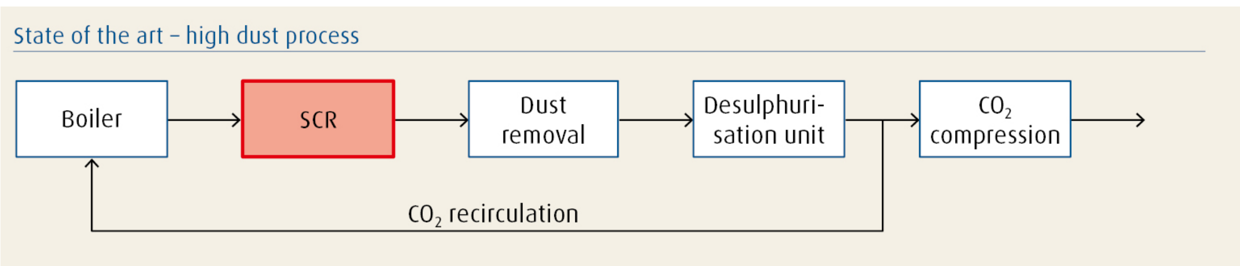
1. Introduction

Carbon dioxide was identified as one of the major green house gases with significant impact on climate. Oxyfuel is one of the three Carbon Capture and Storage (CCS) technologies with a major potential to capture carbon dioxide from fossil fuel fired power plants.

The initial motivation for process development and optimization is the minimization and the control of emissions and the reduction of energy consumption. Several technology routes and variations of process steps have been investigated to remove impurities like NOx, SOx , etc. Especially these impurities are limited for transportation and storage of compressed and purified CO_2.

This paper presents a new concept for the reduction of NOx (NO and NO_2) and simultaneous SOx of a flue gas from an oxyfuel power plant. State of the art in fossil fuel fired power plants is the SCR technology (selective catalytic reduction). This DeNOx unit is normally installed immediately after the boiler in a high dust containing environment at high temperatures of 350 – 400°C and nearly atmospheric pressure. The reduction agent is ammonia or an ammonia-producing derivative like urea. The catalyst life time is limited and the CAPEX is quite high, due to the high atmospheric gas flow. There is a risk for plugging with dust or salts and for corrosion by SO_3-formation. Furthermore the ammonia consumption is increased due to adsorption effects.



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2. LINDE's new concept for DeNOx

The CCS technology offers new possibilities for advanced DeNOX units. The Carbon Dioxide in CCS plants has to be pressurized for the injection, so that new process conditions (high pressure, low temperature) are available for the NOx and simultaneous SOx reduction. The high pressure promotes the oxidation of NO to NO_2 and of SO_2 by NO_2 to SO_3 without any additional catalyst.

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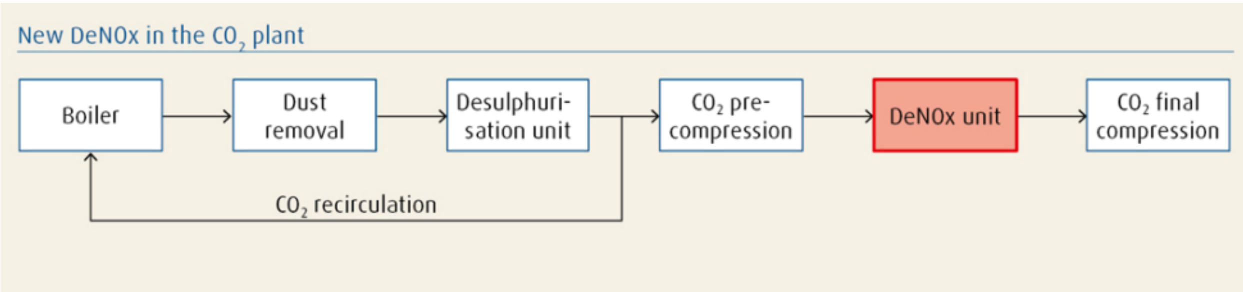
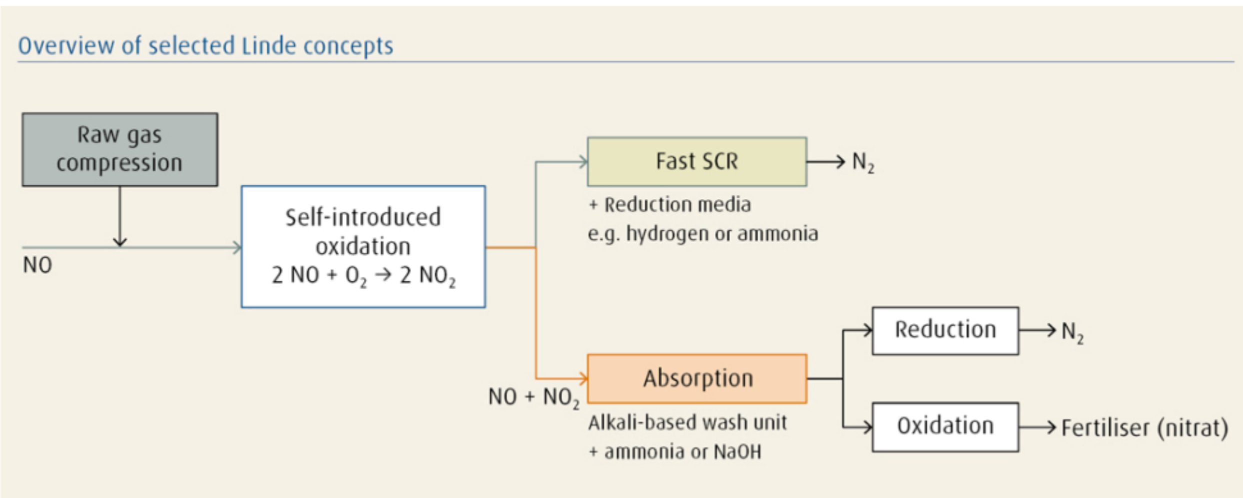
The analysis of different process schemes shows that only the installation of the DeNOx unit under pressure offers significant advantages. In contrast, the SO_2 recovery with a state of the art FGD unit has a lot of advantages compared to a desulphurization under pressure. The state of the art FGD has:

- high sulphur recovery efficiencies
- a long-standing market acceptance
- produces a saleable product (gypsum)
- reducing the sulphur content in the CO_2 recycle back to the oxyfuel boiler and thereby the risk of corrosion in the boiler system.

Under certain conditions a fine purification of SO_2/ SO_3 is required in the CO2-plant to meet the correct quality of the CO_2-product in respect to the total sulphur-content.



Considering all these facts, the technology development was focused on a new DeNOx under pressure.
An overview of the selected LINDE-concepts is given:



Both concepts – the fast catalytic DeNOx and the alkali based wash unit – were investigated in the LINDE R&D laboratories in Pullach/ Germany and confirmed that a conversation and reduction of NOx under pressure is possible. The increase of the reaction pressure up to an optimum has a positive effect on the performance. The cost comparison (CAPEX and OPEX) for commercial plant size was done for the "high dust technology", the fast SCR unit and alkali wash unit located in the CO_2-plant. The preferred DeNOx-process was selected.

Figure 1: CO2 plant in Schwarze Pumpe

The new DeNOx process operates in the range of 10-20 bar in an alkali-based water scrubber. The involved reaction steps for NOx removal are:

- NO Oxidation (atmospheric and under pressure):

$$\mathbf{NO + O_3 \rightarrow NO_2 + O_2} \quad \text{(e.g. WALTER-process)} \quad (1)$$
$$\mathbf{NO + \tfrac{1}{2} O_2 \rightarrow NO_2} \quad \text{(under pressure)} \quad (2)$$

- Water Scrubber for Nitric Acid Production (but the nitric acid produced from NO rich gas needs a continuous oxidation (2) of the released NO):

$$\mathbf{3\,NO_2 + H_2O \rightarrow 2\,HNO_3 + NO} \quad (3)$$

- Alkaline Scrubber (for formation of nitrat with ammonia):

$$\mathbf{NO + NO_2 + 2\,NH_3 + H_2O \rightarrow 2\,NH_4NO_2} \quad (4)$$
$$\mathbf{2\,NO_2 + 2\,NH_3 + H_2O \rightarrow NH_4NO_2 + NH_4NO_3} \quad (5)$$
$$\mathbf{NH_4NO_2 + 1/2\,O_2 \rightarrow NH_4NO_3} \quad \text{or} \quad (6)$$
$$\mathbf{NH_4NO_2 \rightarrow N_2 + 2\,H_2O} \quad \text{(decomposition > 60°C)} \quad (7)$$

The conventional NO oxidation stage (1) is no longer needed. The NO_2 is formed by oxidation of NO under pressure and oxygen (2). Based on this, a new concept for NOx or simultaneous NOx / SOx removal (8; 9) can be realised.

$$\mathbf{SO_2 + 2\,NH_3 + H_2O \rightarrow 2\,(NH_4)_2SO_2} \quad \text{and} \qquad (8)$$
$$\mathbf{SO_3 + 2\,NH_3 + H_2O \rightarrow 2\,(NH_4)_2SO_4} \qquad (9)$$

3. Realisation and testing of the new DeNOx in the pilot plant

The next step was the validation of these lab results using synthetic flue gas in a pilot plant with real flue gas from a lignite fired oxyfuel boiler. For this reason a new pilot scrubber was integrated in the CO_2 unit at Vattenfall's Oxyfuel pilot plant at Schwarze Pumpe (figure 1).

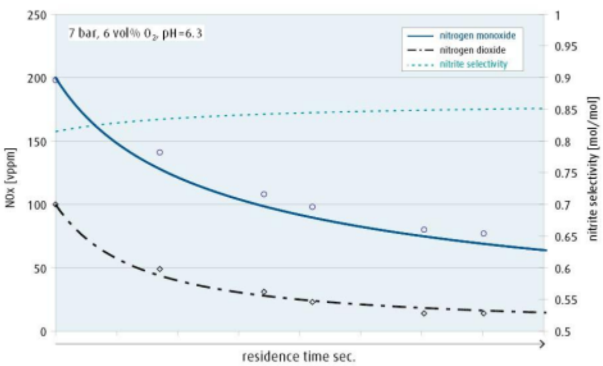
The start-up of this DeNOx-test plant was done in July 2010.

The following influences have been investigated at first in the laboratories and then in the test modul in the oxyfuel pilot plant in Schwarze Pumpe:

- NOx removal rate depending on washing media (NH_3; NaOH)
- NOx removal rate depending on pressure, temperature, pH-value and residence time
- Nitrate, Nitrite formation depending on NO/ NO_2 ratio (4; 5)
- Nitrite decomposition (regeneration) (7)

The reduction of NOx in the alkali wash scrubber was successful tested under real gas and process conditions in the oxyfuel pilot plant Schwarze Pumpe (diagram 1, 2, 3):

Diagram 1 and 2: Simulation and comparison with measured data



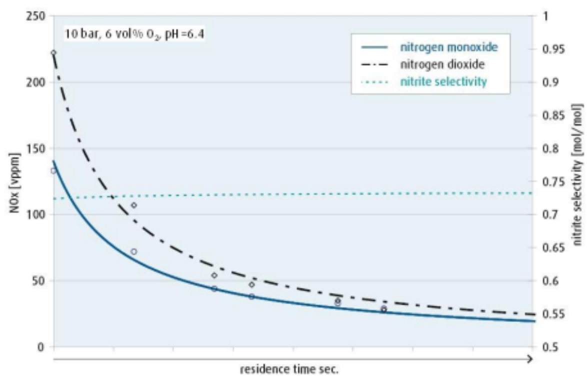
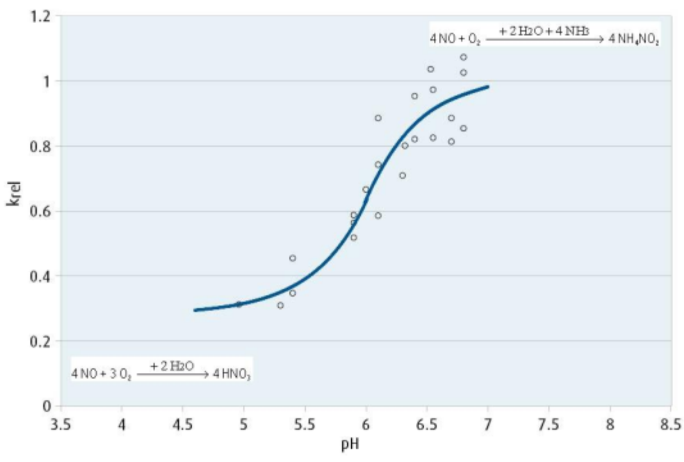


Diagram 3: NO conversion rate depending on pH



4. Advantages of the new LINDE DeNOx

The new process has a couple of advantages compared to the existing hot SCR technology (state of the art):

- reduced gas flows (three times lower, SCR is arranged after boiler, were the gas contains the recycle gas)
- the gas is treated regarding SO_2, dust; therefore the process conditions are "mild" compared to the "high dust" catalytic DeNOx
- gas flow is compressed, so that smaller equipments can be used
- an alkali-based solvent has a significantly better capability for the removal of NOx compared to water and no complete oxidation of NO is needed.
- a simultaneous SOx and NOx removal is possible; SO_2 adsorption is independent of the NO kinetics and can directly be removed along with SO_3; an oxidation is not required
- it is possible to use relatively cheap construction materials due to the avoidance of acid formation
- there is a potential for regeneration of the washing media or the oxidized washing media can be used e.g. as a fertilizer

The newly developed DeNOx unit has reduced invest- and operational costs and leads to a further optimization of the overall oxyfuel technology. This new process is patented by Linde and will be commercialized after successful pilot plant results under the trademark LICONOX (Linde Cold DeNOx). The next step is the integration in the CO_2 processing unit in the demonstration plant.