NOx processing experiences for removal in the CO2 plant in the Oxyfuel combustion process

Roland Ritter a,*, Torsten Stoffregen a, Nicole Schödel b, Florian Winkler b

a Linde Engineering Dresden GmbH, Bodenbacher Str. 80, 01277 Dresden, Germany
b Linde AG Linde Engineering Division, Dr.-Carl-von-Linde-Str. 6-14, 82049 Pullach, Germany

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1. Introduction

Flue gas purification is a necessary method to avoid emission of sour gases like SOX and NOX into the environment. An other important aspect is the reduction of CO2 emission from coal-fired power plants. Oxyfuel technology is one of the CCS technologies to reach this goal. Linde Engineering Dresden in cooperation with Vattenfall Europe is operating a CO2 pilot plant producing liquefied carbon dioxide as part of the Oxyfuel pilot plant at Schwarze Pumpe. Special requirements for product specification and material selection make a flue gas purification regarding SOX and NOX unavoidable. The oxyfuel technology offers new process conditions for flue gas cleaning which are not available at atmospheric conditions.

The CO2 processing of the Oxyfuel process offers a wide range of temperature (with warm-up during compression; 30 °C 120 °C) and pressure conditions (maximum up to required pipeline pressure or liquefaction pressure; preferred 5 … 40 bar). At these conditions, the auto oxidation of NO into NO2 is induced and also the oxidation of SO2 into SO3 with existing NO2.

This circumstance was the basis of a technology screening for NOX and SOX removal systems from flue gas of Oxyfuel processes at Linde. At Linde laboratories, catalytic and non-catalytic DeNOx and DeSOx processes have been investigated for Oxyfuel application.

* Corresponding author. Tel.: +49-351-250 3267; fax: +49-351-250 4805.
E-mail address: roland.ritter@linde-le.com
2. Linde’s way of development for removal of NOx and SOx

At first the catalytic reduction with ammonia, ammonia derivates or hydrogen as reduction media has been studied at Linde laboratories. The economic evaluations have not shown extensive benefits compared to atmospheric SCR technologies, therefore this technology was not pursued at pilot scale.

In parallel to the SCR technology for removal of NOX, a wet purification system was investigated at Linde laboratories for removal of SOX. A state of the art technology of wet/semi dry purification systems is the gypsum production with limestone and SO2. This technology is the common process for flue gas desulphurisation (FGD) and state of the art.

After the first feasibility studies, laboratory experiments and economical evaluations, it was decided to develop a process on wet alkaline scrubber system to remove NOX from pressurized flue gas, simultaneously removing of SOX. The high pressure promotes the oxidation of NO to NO2 and of SO2 by NO2 to SO3 without any additional catalyst.

\[ 2 \text{NO} + \text{O}_2 \rightarrow 2 \text{NO}_2 \]
\[ \text{SO}_2 + \text{NO}_2 \rightarrow \text{SO}_3 + \text{NO} \]

3. Realisation and testing of DeNOx in the pilot plant

After demonstration of the single process steps on laboratory scale, a pilot scrubber was erected and commissioned at Schwarze Pumpe Oxyfuel pilot plant in 2010.

Pilot plants test have been performed in July up to September 2010. Several parameters influences have been determined like pressure, temperature, pH-value of the washing media. The first test campaign was carried out with ammonia water as the alkaline wash solvent. A kinetic model was created to describe the system of NOX absorption in an alkaline media. Especially the calculation for nitrite selectivity of the system with ammonia water was integrated in the model. Column profiles regarding NO and NO2 have been recorded for comparison of the absorption rate for tetravalent nitrogen oxides and N2O3 with the observed absorption rates with NH3 as washing media. The ammonium nitrites are formed from NO during alkaline scrubbing of oxygen containing flue gas.

\[ \text{NO} + \text{NO}_2 + 2 \text{NH}_3 + \text{H}_2\text{O} \rightarrow 2 \text{NH}_4\text{NO}_2 \]
\[ 2 \text{NO}_2 + 2 \text{NH}_3 + \text{H}_2\text{O} \rightarrow \text{NH}_4\text{NO}_2 + \text{NH}_4\text{NO}_3 \]
The ammonia water can also react with the SOX simultaneously, so that SOX can be removed in the same purification step.

\[
\begin{align*}
\text{SO}_2 + 2 \text{NH}_3 + \text{H}_2\text{O} & \rightarrow (\text{NH}_4)\text{SO}_3 \\
\text{SO}_3 + 2 \text{NH}_3 + \text{H}_2\text{O} & \rightarrow (\text{NH}_4)\text{SO}_4
\end{align*}
\]

In May 2011 a temporary continuous reduction reactor was installed to proof the concept of the nitrites reduction into nitrogen.

\[
\text{NH}_4\text{NO}_2 \rightarrow \text{N}_2 + 2 \text{H}_2\text{O} \quad \text{(decomposition)}
\]

Flow diagram of LICONOX with reduction unit

The conversion degree of ammonium nitrite into nitrogen has been determined and the reaction gas has been analysed for complete nitrogen balance. The results have been fed into a kinetic model for later process description and scale-up. The selectivity of nitrite production can be influenced by optimisation of the process parameter especially the system pressure. With the high selectivity and the decomposition step the by-product can be reduced to less than 25%.

In the next test campaign the washing media was changed from ammonia water to NaOH to investigate the NOX removal with this solvent. In principle the NaOH is a washing media which is able to remove the NO and NO2.

\[
\begin{align*}
2 \text{NO} + \text{O}_2 + 2 \text{NaOH} & \rightarrow \text{NaNO}_2 + \text{NaNO}_3 + \text{H}_2\text{O} \\
2 \text{NO}_2 + 2 \text{NaOH} & \rightarrow \text{NaNO}_2 + \text{NaNO}_3 + \text{H}_2\text{O}
\end{align*}
\]

4. Next steps

The piloting of the Cold DeNOx is finished. Based on these pilot plant data an up scale of the scrubber for a demonstration plant is possible. The newly developed DeNOx unit has reduced investment and operational costs and leads to a further optimisation of the overall oxyfuel technology. This DeNOx process is now marketable under the trademark LICONOX™ (Linde Cold DeNOx).