Flue Gas Cleaning for CO₂ Capture from Coal-fired Oxyfuel Combustion Power Generation

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Abstract

Current progress in flue gas cleaning for CO₂ capture from oxyfuel combustion has been described based on conceptual development, fundamental understanding and practical tests at the Schwarze Pumpe Oxyfuel Pilot Plant (OxPP). Significant improvement in understanding the characteristics of SOₓ, NOₓ, particulate matters (PMs) and non-condensable gas components in flue gas cleaning processes provide a scientific basis for further developments of flue gas cleaning technologies. Testing results from pilot studies have proved that flue gas cleaning systems have reached the achievable performance and have also shown that there is generally no fundamental technical bottleneck for most of the flue gas cleaning technologies. Further developments should focus on comprehensive optimisation of the flue gas cleaning processes combined with boiler and downstream CO₂ compression processes. Changes in flue gas cleaning technologies may be excepted if more attractive gas cleaning processes could be successfully developed in the near future; for example, NOₓ removal and control technologies. The development of a monitoring approach for the mitigation of non-condensable gases is an important operational issue for large-scale oxyfuel combustion plant.

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1. Introduction

Compared to other CO₂ capture technologies (post-combustion and pre-combustion) for coal-fired power generation, the oxyfuel combustion CO₂ capture is a CO₂ enrichment approach not a CO₂ selective method [1]. Therefore, the main purpose of flue gas cleaning is to control the non-CO₂ components for both CO₂ capture and the boiler operation, instead of a pretreatment procedure for the selective capture of CO₂ from flue or fuel gases. The development of flue gas cleaning for oxyfuel combustion CO₂ capture has been closely linked with the development

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of up- and down-stream processes i.e. oxyfuel combustion and CO₂ processing in Vattenfall since 2002 [2,3,4,5]. The initial conceptual development had its focus on available technologies for demo plant applications, potential issues to be handled for oxyfuel combustion, design criteria and techno-economic optimisation of the cleaning system based on available data and experiences. The results of the conceptual development have been considered as inputs for pilot project studies and further development of the flue gas cleaning system for demo plants. This paper is a summary of the current progress in this area.

Figure 1. General set-up of flue gas cleaning system for coal-fired oxyfuel combustion and major processes

Figure 2. Working map for the development of flue gas cleaning system
Although there are several technical options for the flue gas cleaning and system configuration, the basic set-up of the system for testing and proof of the performance are shown in Figure 1, from which most of the issues identified from the conceptual study could be investigated and the results could be applied for most of the other options. A working map has been set up for development of the flue gas cleaning system and for the pilot plant studies at the Oxyfuel Pilot Plant (OxPP). In this working map, the main tasks have been identified for the development of basic unit operations. Flue gas cleaning is linked to the downstream CO$_2$ processing. Therefore, a comprehensive consideration of the whole capture chain has been taken into account.

In the following sections, the main progress in the development of flue gas cleaning systems is presented in terms of important gas components – SO$_x$, NO$_x$, particulate matters (PMs) and non-condensable gases, mainly N$_2$, O$_2$ and Ar. Important issues identified from the development will be discussed based on the individual gas cleaning processes and various options.

2. SO$_x$ Behavior and Removal

The development of SO$_x$ removal for flue gas cleaning has been focused on the understanding of SO$_x$ behavior during oxyfuel combustion, achievable performance of the de-SO$_x$ processes and the downstream gas quality requirement (limitations) of SO$_x$. The possibility of de-SO$_x$ in a pressurised CO$_2$ processing system was also investigated. Knowledge obtained from actual technical developments aimed providing a scientific basis for flue gas cleaning specifications I & II as shown in Figure 2.

The flue gas recycle (FGR) has a significant impact on sulphur retention in the boiler, which in turn affect the SO$_x$ behaviour and removal, because more than the double amount of the fuel sulphur may be returned to furnace by the FGR. The SO$_x$ behaviour in the FGR has been investigated based on the general set-up of the flue gas system shown in Figure 1 with hot flue gas recycle. The investigation was performed at the OxPP with a variation of O$_2$ concentration in the oxidant, which requires different amounts of FGR. As shown on the left side of Figure 3, the reduced total flue gas volume flow did not increase the SO$_2$ concentration in the FGR when the O$_2$ concentration in the oxidant was increased from 24 to 32 vol% wet. The SO$_2$ concentration was stabilised by certain retention mechanisms, which may be fuel property dependent. A comparison of sulphur removal performed on different lignite and combustion conditions (oxyfuel and air-firing) is shown on the right side of Figure 3 based on sulphur balance analyses. In comparison to air-firing, the sulphur retention in the boiler has been enhanced during the oxyfuel combustion. For example, the percentages of fly ash retention and the potential of deposits (sulphur captured in deposit combined with measurement uncertainties) were increased during the oxyfuel combustion. This is important for the consideration of a tolerant sulphur level in the FGR combined with boiler design and boiler operation, i.e. to define the flue gas cleaning specification I for FGR.

The SO$_2$/H$_2$SO$_4$ concentration in flue gas has been investigated for oxyfuel combustion of lignite and then compared to air-firing. Initial measurement results have shown that the measured conversion ratios of SO$_2$ to SO$_3$ at the outlet ESP are fuel dependent as shown in Figure 4. Ash properties have strong impacts on the SO$_2$/H$_2$SO$_4$ concentrations at the outlet of ESP. It is expected that significant retention of SO$_2$/H$_2$SO$_4$ by the ashes was carried out from the furnace to the end of the ESP based on the observed sulphur level in the ashes at different locations. Relatively higher concentration of SO$_2$/H$_2$SO$_4$ was determined at a higher temperature window (around 400 °C). It is consistent with the observation from University of Utah [6]. The formation of SO$_2$/H$_2$SO$_4$ and the retention processes are still under investigation.

A modified wet limestone/gypsum FGD process with an external oxidation reaction tank was used for the removal of SO$_x$ as well as other acidic gases. A flue gas condenser with alkaline chemical (NaOH) dosing was used to remove moisture and also used as a polishing step for further removal of acidic gases. Good performance of acidic gas removal has been achieved under oxyfuel combustion conditions without any fundamental problems [7]. The achievable concentrations of the acidic gas components in the clean gas after FGC under the testing conditions
could be: $\text{SO}_2 < 10 \text{ mg/Nm}^3$, dry; $\text{SO}_3 < 10-30 \text{ mg/Nm}^3$, dry (with some measurement uncertainty); $\text{HCl}$ and $\text{HF} < 1 \text{ mg/Nm}^3$, dry (with some measurement uncertainty).

![Figure 3. SO$_2$ behavior and removal from oxyfuel combustion flue gas (left: S behavior in FGR corresponding to FGR flow rates; right: relative removal/retention of S within the boiler and through flue gas cleaning processes)](image)

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![Figure 4. Fuel and SO$_2$ concentration dependence of SO$_3$/H$_2$SO$_4$ conversion in lignite combustion (measured at the outlet of ESP)](image)

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3. NO$_x$ Characteristics and Reduction

As shown in Figure 2, there are more options for NO$_x$ removal and reduction within the CO$_2$ capture processes compared to conventional solutions for utility boilers. The understanding of NO$_x$ behavior in oxyfuel combustion and gas processing unit (GPU) is an important task for the development of flue gas cleaning. NO$_x$ behaviour in the CO$_2$ capture chain has been characterised at the OxPP, which includes NO$_x$ formation/reduction in boiler and conversion, absorption and adsorption in the flue gas path, as well as FGD, FGC and GPU. The comprehensive investigation provides a scientific basis for the handling of NO$_x$ issues, and also for the optimisation of NO$_x$ removal and reduction within the CO$_2$ capture chain.

Although the optimisation of primary NO$_x$ reduction is still an ongoing task in the oxyfuel combustion pilot, there was a significant reduction of NO$_x$ formation in the oxyfuel combustion in comparison to air-firing. The conversion of NO to NO$_2$ from the outlet of the furnace to the end of FGC was not very significant. Therefore, the possibilities for the removal of NO$_x$ are limited by using the conventional wet scrubbing process. Generally, NO$_x$ has no significant impacts on the boiler operation, except for emission related issues. Therefore, they have less influence on the flue gas cleaning specification I. Instead, the requirements of the flue gas cleaning specification II...
for NO\textsubscript{x} should be compromised with the downstream specifications for CO\textsubscript{2} processing as shown in Figure 2 and described below.

Significant conversion of NO to NO\textsubscript{2} as well as absorption and adsorption of NO\textsubscript{x} have been observed in the CO\textsubscript{2} compression process [8]. These provide more opportunities for NO\textsubscript{x} removal and reduction, but it also can generate new operational issues for the handling of NO\textsubscript{x} components during the processes. Therefore, NO\textsubscript{x} in oxyfuel combustion CO\textsubscript{2} capture processes should be handled as both environmental (emissions and by-products) and operational issues.

The optimisation of NO\textsubscript{x} reduction/removal is a more complicated task in comparison with those for conventional coal-fired power plants, because of more available options and specific operational issues. Figure 5 shows an estimation of NO\textsubscript{x} reduction requirements based on the non-optimised NO\textsubscript{x} levels generated from the oxyfuel combustion pilot, as well as current and future NO\textsubscript{x} emission regulations (200 and 100 mg NO\textsubscript{x} (as NO\textsubscript{2})/Nm\textsuperscript{3} dry for plants > 300 MW\textsubscript{th}), which are converted to fuel basis in Figure 5). It reveals that more reduction of NO\textsubscript{x} is expected when the combustion is optimised for NO\textsubscript{x} reduction; a concentration of about 200 mg/Nm\textsuperscript{3} should be achievable, but this is yet to be proven. A comparison of the gas volume flow rates at various potential locations for the NO\textsubscript{x} reduction is shown in Figure 5 (right) as well. As shown in the figure, less than 60% of NO\textsubscript{x} reduction may be required for future strict air emission limits (corresponding to 100 mg NO\textsubscript{x}/Nm\textsuperscript{3} dry) based on a non-optimised NO\textsubscript{x} generation level (which can be further reduced). It has been observed that more than 60% of the the conversion of NO to NO\textsubscript{2} followed by the removal of NO\textsubscript{2} by absorption in condensate is not very difficult in pressurised CO\textsubscript{2} processing processes. There are more options for the removal of NO\textsubscript{x} in the GPU, which could be applied to easily achieve the air emission requirements in comparison to traditional SCR. SCR has disadvantages while handling large volumes of gas that have high dust contents (as shown on the right of Figure 5). Using SCR for NO\textsubscript{x} reduction also presents a loss of the advantage of oxyfuel with the primary de-NO\textsubscript{x} function (re-burning recycled NO\textsubscript{2}). A simple solution for air emission is less important than the development of compression and dehydration processes for the easily handled NO\textsubscript{x} issues in combination with the reduction of NO\textsubscript{x}. While developing the GPU NO\textsubscript{x} removal options, it is important to consider additional issues such as corrosion potential and by-product handling.

![Figure 5. Comparison of NO\textsubscript{x} reduction requirements downstream of flue gas cleaning with the air emission limits on the fuel energy input basis and the actual volume flow rates of the flue gas at various locations (based on presently measured NO\textsubscript{x} levels in the OxPP at FGC exit, without combustion optimisation to reduce NO\textsubscript{x} and without SCR or other technology for secondary NO\textsubscript{x} removal).](image-url)

The development of de-NO\textsubscript{x} in CO\textsubscript{2} purification processes is in progress. Two slip-stream de-NO\textsubscript{x} processes were designed by the GPU suppliers (Air Products and Linde) for testing at the OxPP. One of the pilot scale test units is presently being performed (Linde), while the other is under construction and will be commissioned in November 2010. The test results will be used for the understanding of NO\textsubscript{x} behaviour in pressurised processes, and also for the design and further development of large-scale processing units. Gas cleaning specifications for GPU as indicated in
Figure 2 will be developed based on both experiences from the tests, as well as from increased theoretical knowledge. The investigations will also be related to critical issues scaling up equipments. A comprehensive optimisation of the de-NOx processes will be based on the test results for the pressurised de-NOx combined with an evaluation of NOx reduction in the boiler.

4. Particulates Matters (PMs) and Control

Different options of PMs removal from coal-fired oxyfuel combustion flue gas have been studied in collaboration with equipment suppliers [9]. The investigated options include cold-side and hot-side ESPs, fabric filter (bag houses) combined with various configurations in terms of flue gas recirculation and heat integration. The general conclusion of the studies reveals the need to further investigate the actual performance of cold-side ESP under oxyfuel combustion conditions in order to reduce the uncertainty for comparison of different options.

A three-field pilot-scale ESP has been tested for dust removal from oxyfuel combustion of lignite at the OxPP. The performance of the ESP was evaluated under the oxyfuel combustion and compared to air-firing conditions. The ESP performance improved under oxyfuel combustion conditions. A ~50% higher voltage could be applied under oxyfuel combustion conditions in comparison with air-firing. In addition, more stable ESP operation has been observed under oxyfuel combustion conditions. The variation of operation current and voltage under oxyfuel combustion were much smaller in comparison with air-firing. Better performance achieved during oxyfuel combustion conditions was most likely due to higher levels of moisture, SO2 and SO3/H2SO4 in the oxyfuel combustion flue gas. The contents of S, Fe, Na and K in the fly ashes showed a tendency towards higher values under oxyfuel combustion conditions. The measurement results showed that the ash resistivity was on the same level in the 1st field under both oxyfuel combustion and air-firing conditions. More than one order of magnitude lower ash resistivity was found in the 2nd field under oxyfuel combustion conditions compared with air-firing. The ash resistivity from air-firing and in particular from oxyfuel combustion fulfilled properties required for a high-performance electrostatic precipitation [10].

It is generally considered that a better performance could be achieved under oxyfuel combustion conditions for the same fuel. There should be no fine ash accumulation in the recycle flue gas if the ESP performance to be as effective as the ESP used at the OxPP. No negative impacts on ESP performance were observed under the higher CO2 concentration during the oxyfuel combustion conditions.

Different levels of particulate matters were determined for the clean gas after FGD and FGC. The results indicated that most particulate matters did not come from fly ashes. The particulate matter control for downstream processes flue gas should pay more attention to particle emissions from the process itself. A careful design of mist eliminator for FGD and FGC systems is the most important measure to control the PM to an acceptable level for GPU. Reducing the PMs generated from downstream processes such as corrosion products is also important for achieving a lower level of PMs in the clean gases.

Compared with the fly ash removal through ESP, fabric filter removal of fly ash has an additional advantage on the effective removal of SO3/H2SO4 from flue gas. Test results have shown that the concentration of SO3/H2SO4 could be significantly reduced by the dust (ash) cake formed on the surface of the fabric filter. The removal efficiency was highly dependent on ash properties such as the content of alkaline components. It is expected that the SO3/H2SO4 removal efficiency could be maintained through alkaline sorbent injections for the ashes with low content of alkaline components. A joined test program on sorbent injection for SO3/H2SO4 mitigation under oxyfuel conditions is in progress.

5. Non-condensable Gas Components and Mitigation

As mentioned before, the non-condensable fraction of the flue gas generated from oxyfuel combustion consists of Ar, O2, N2 and other minor gas components such as CO and NO. Impacts of non-condensable gases on CO2 capture
have been studied in Vattenfall from the following aspects: the properties of non-condensable gas components and influence on CO₂ compression and purification [11, 12]; techno-economic evaluation of the impacts of non-condensable gas components on CO₂ capture, transport and storage [13]; CO₂ quality requirements for non-condensable gas and scientific basis [3], and practical mitigation approaches for demo plant which is ongoing at the OxPP. In addition, changes and reactions of the non-condensable gas components in flue gas cleaning and CO₂ processing processes have also been studied.

The non-condensable gas components have complicated impacts on the CO₂ capture, transport and storage, depending on the properties of the gas components and the processes. The most important impacts could be categorised as: energy consumption for separation, CO₂ loss during the separation (CO₂ capture rate), volume and thermodynamic properties of CO₂ mixtures (on transport and storage), and special concerns such as corrosions (O₂), emissions (CO and NO), and health and safety during accidents (most of the components). For CO₂ storage, the investigations were performed on reactions with rock and saline water and its impact on storage containment and injectivity.

The sources of non-condensable gases in the oxyfuel combustion CO₂ capture processes mainly come from oxidant (O₂ purity), combustion process (excess O₂, CO, NO etc.) and air in-leakage. The air in-leakage is the main source of the non-condensable gases and should be mitigated to as low levels as possible.

In the design phase, several measures have been applied to reduce the air in-leakage into the OxPP. The plant is designed with two induced draft fans in order to avoid a high under-pressure after a single fan. Furthermore, the plant uses a sealing gas system where dry flue gas is recycled back to the boiler after the FGC. The sealing gas is used, for instance, either in order to seal the passage of sootblowers and water lances through the waterwall or to purge the several ash discharge airlocks. The ash removal system is designed with a special sealing system for both the boiler and the ESP. An external oxidation tank was designed for the wet limestone/gypsum FGD system. The main purpose of the external oxidation is to avoid the mixture of oxidation air with the clean flue gas entering the downstream processes. These measures have significantly mitigated the air in-leakage into the CO₂ capture chain. The results indicated that the CO₂ concentration could be kept at above 85 vol% on dry basis for most oxyfuel combustion operation periods. The total air leakage is estimated to be below 1.5 mass% of the flue gas flow rate at the outlet of furnace.

In addition to these design features the prevention of air in-leakage should not only be a crucial issue in the design of the power plant but also during the operation. Any ongoing degradation of the process in terms of leakage air needs to be detected as fast as possible to initiate appropriate maintenance measures. Thus, one of the major goals for a process monitoring system for large-scale oxyfuel boilers is the identification and localisation of air in-leakages. This issue will be addressed in our ongoing research [14] in order to enable the operation of the process as close to its maximum efficiency as possible. The investigations are based on an experiment conducted in the OxPP. During the test leakage, air was dosed into the process at several locations that were characteristic for leakages. The process data gathered in this experiment were analysed by means of a principal component analysis. This approach was found to be a promising method for monitoring of oxyfuel power plants with regard to increasing air in-leakages. It is possible to apply appropriate data-based monitoring measures not only for an identification of occurring leakages but also for a localisation of the leakage. In addition, the data-based methods shall be further improved and tested on-line.

6. Conclusions

No fundamental technical problems have been identified for the removal of SOₓ and PMs by using current available flue gas cleaning technologies such as wet FGD and ESP. Flue gas cleaning for NOₓ removal should be further developed with a comprehensive optimisation of various technical options applied in furnace, gas cleaning and CO₂ processing processes. Further development of flue gas cleaning processes should focus on the confirmation of flue gas cleaning system capabilities for various fuels and operation conditions; techno-economic optimisation of
the flue gas cleaning systems, further reducing the energy consumption and costs, and validation of the achievable performance in large-scale systems. Development of monitoring approach for the mitigation of non-condensable gases is an important operation issue for large-scale oxyfuel combustion plant.

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8. References

1. Anheden M; Yan J, De Smedt G. Denitrogention (or oxyfuel concepts). Oil & Gas Science and Technology - Rev. IFP, 60 (3): 485-495, 2005.