Available online at www.sciencedirect.com
ScienceDirect
Energy Procedia 63 (2014) 463 – 470
Energy Procedia

GHGT-12

Performance simulation of full-scale wet flue gas desulfurization for oxy-coal combustion

Thibaut Neveux[a,]* , Hayato Hagi[a,b], Yann Le Moullec[a]

[a]EDF Research & Development, 6 quai Watier, F-78400 Chatou, France
[b]MINES ParisTech, PSL – Research University, CES – Centre for energy efficiency of systems, 60 Bd St Michel, F-75272 Paris Cedex 06, France

Abstract

Oxy-coal combustion implies significant changes on the power plant design and operation compared to air-firing. In particular, the new operating conditions cause modifications on the process design and performance of the wet flue gas desulfurization (FGD) unit. It has been previously showed at pilot plant scale that high SO_2 removal efficiency is achieved and no substantial problems have been observed while operating in oxy-combustion conditions. This study intends to meet the needs for a full-scale analysis of the process performances in order to investigate the wet FGD potential. To do so, a dynamic model already developed in a previous work for air-fired power plants has been adapted to deal with these new process conditions and used to perform an investigation of the wet FGD capability when operating under oxy-combustion conditions.
The process design and operating parameters are determined to optimally achieve process performances (energetic, economics). There is no significant difficulty to achieve targeted performance. A conservative SO_2 outlet of 200 mg/Nm^3 can be achieve easily both for low and high sulfur coal. Warm recycle increases the oxy-combustion power plant efficiency, reduces the flue gas to be treated but increases the SO_2 content by 60 %. To cope with this increase inlet SO_2, the L/G ratio is increased by 80 %; but the investment cost is reduced by 25 % compared with cold recycle. Finally, a global design of the FGD+DCCPS equipment is needed in order to achieve optimal performance of the flue gas desulfurization at reasonable cost.

Peer-review under responsibility of the Organizing Committee of GHGT-12

Keywords: oxy-combustion, desulfurization, process simulation, FGD modelling

* Corresponding author. Tel.: +33-1-30-87-85-69.
E-mail address: thibaut.neveux@edf.fr

Peer-review under responsibility of the Organizing Committee of GHGT-12
doi:10.1016/j.egypro.2014.11.049

1. Introduction

Oxy-coal combustion implies significant changes on the power plant design and operation. Among issues to be tacked with, the flue gas cleaning steps are strongly affected by the differences between air- and oxy-combustion flue gases. In particular, the wet flue gas desulfurization (FGD) unit operates at higher temperature, with a reduced flue gas flow rate by 50-60 % and a different inlet flue gas composition. The CO_2 partial pressure is higher (around 60 $\%_{vol, wet}$) as well as the H_2O partial pressure (up to 30 $\%_{vol}$) and the SO_2 concentration (up to 5 times the air-fired concentration, depending on cold or warm recycle).

These new operating conditions cause modifications on the desulfurization process design and performance. These conditions have already been experimentally tested on small pilot plants, e.g. at the 30 MW_{th} oxy-combustion pilot plant in Schwarze Pumpe [1], and it has been showed that high SO_2 removal efficiency is achieved and no substantial problems have been observed while operating in oxy-combustion conditions. However, despite the fact that several operating conditions have been tested, there is still a room for a full-scale analysis in order to investigate the wet FGD potential. Consequently, this study intends to predict the process performances for a full-scale coal fired power plant (1 GW_e), in particular in terms of separation efficiencies, gypsum quality, limestone consumption, pumps electrical consumption, equipment size and costs. The different design and operating parameters of the FGD unit are looked into; aiming to optimize them with respects to energetic and economics performances.

In order to do so, a dynamic model already developed in a previous work [2] for air-fired power plants has been adapted to deal with these new process conditions. To be used in oxy-combustion conditions, the model has been adapted to consider the effect of temperature and higher CO_2 partial pressure on FGD chemistry, and a separated oxidation tank is used to avoid flue gas dilution by air.

2. Modeling of wet FGD

2.1. Previous model development

A dynamic phenomenological model of wet limestone/gypsum FGD has previously been developed [2] and more specially adapted for the wet limestone/gypsum FGD operated by EDF. This model is used to anticipate the evolution of regulatory context regarding emission limit of SO_2 for coal-fired boilers, as well as to assist engineers in studying industrial issues. This model represents the spray and bubble hydrodynamics respectively in the absorption zone and the oxidation tank. Transfers between gaseous, liquid and solid phases are taken into account as well as a detailed liquid chemistry with the main chemical equilibria and non-ideal thermodynamics. The three kinetic reactions involved in FGD chemistry are modeled: limestone dissolution, sulfites oxidation and gypsum precipitation. The gypsum quality is also represented, considering the residual limestone and the fly ashes collected by the spray. The developed model answered most of the needs for the study of FGD performance in different scenarios: coal or limestone substitution, denitrification or dust removal operational problems, modification suggestions and determination of new operating parameters.

2.2. Adaptation for oxy-combustion combustion

The oxy-combustion conditions imply numerous changes on the combustion and the cleaning steps. The previous model was not developed for those conditions, requiring some adaptations on the phenomena modeling. In particular, the overall performances are affected in several ways [3]: external oxidation, different flue gas flow rate and composition, increased FGD operating temperature, reduced limestone dissolution rate. First of all, the oxidation reactor has to be separated from the absorber in order to avoid flue gas dilution by air (see Figure 1). In the model, the gas connectivity between these the absorption tower and oxidation tank is removed. Since the combustion is realized in a nitrogen depleted, the flue gas flow rate is reduced compared with air-fired combustion. This leads to a higher SO_2 content in flue gas, which affects the driving force and the ratio of film resistances. The recycle of CO_2 in the boiler to limit flame temperature also increase the CO_2 content (up to 60 $\%_{vol, wet}$). This higher CO_2 content could acidify the slurry and affects its chemistry. Since all mass-transfer limitations and chemical equilibria were already implemented in the previous model, the only adaptation performed related to flue gas composition is the addition of an enhancement factor for CO_2 absorption using the kinetic of Pinsent et al. [4] as function of temperature and hydroxide ion concentration.

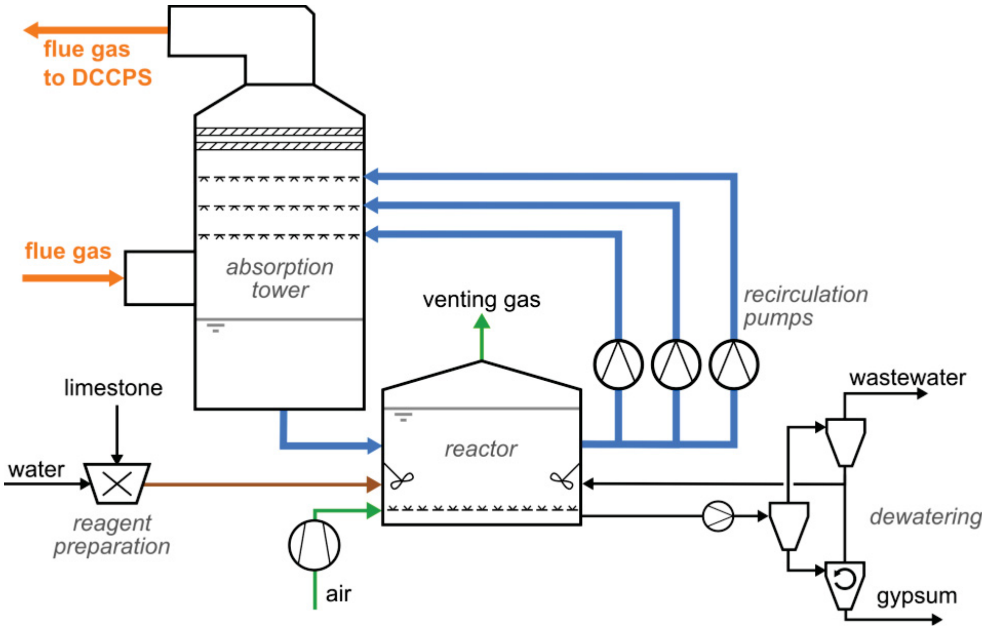

Figure 1. Simplified flow scheme of the wet FGD process adapted for oxy-combustion

Due to the higher water (up to 30 $\%_{vol,\ wet}$) and SO_2 content in flue gas, the operating temperature of FGD is expected to be higher than 45°C, the typical operating temperature encountered in classic wet FGD. Depending on warm/cold recycle and type of coal (e.g. lignite or bituminous), the operating temperature can vary between 40 and 70 °C, this value can be calculated by a heat balance knowing the flue gas temperature, flow rate and composition. This increase in operating temperature affects every phenomenon in the FGD system: gas solubilities are reduced; mass-transfer is increased (higher diffusivities, lower viscosities); both limestone and gypsum solubility constants are reduced and both kinetics are increased. Gypsum precipitation is expected to be facilitated at higher temperature but not limestone dissolution. Limestone has a lower solubility but the pH decreases due to CO_2 absorption could help its dissolution. All these aspects should be considered in the new model to properly simulate the slurry chemistry.

All the physico-chemical properties are calculated according to temperature so that no particular adaptation is required for gas solubility (Henry's constant) and mass-transfer (properties and hydrodynamics correlations). It is however necessary to adapt the chemical kinetics since most of studies dedicated to wet FGD chemistry are performed between 40 and 50 °C and few data on FGD chemistry exist at higher temperature. Kinetics have been modified using existing laws around 45 °C and activation energies reported in literature for sulfite oxidation [4], gypsum precipitation [5] and limestone dissolution [6]. Dissolution thermodynamic constants have been modified using Gibbs free energy of reaction [7]. Such adaptation is enough for this exploratory study; the different model would need to be validated against laboratory data for a proper representation of slurry chemistry at higher temperatures.

To sum up, relatively few modifications have been made on the model to be suited for oxy-combustion conditions: separation of oxidation tank, higher absorption of CO_2, adaptation of kinetics and equilibrium constants with respect to temperature.

3. Comparison with experimental data

3.1. Validation against industrial data in air firing condition

The model results have been successfully validated against full-scale industrial data from a 600 MWe coal-fired power plant located in Cordemais (France) owned and operated by EDF. Several tests were performed in controlled and monitored conditions between 2007 and 2009, aiming to analyze the effect of slurry pH (from 5.1 to 5.8) and L/G ratio (permutation of three spray levels). The models shows an excellent agreement with the industrial data since the average relative deviation between simulated and experimental removal efficiencies is less than 1.5 % for the controlled industrial tests (see Figure 2). The increase of desulfurization degree due to pH or L/G increase is accurately represented. In addition, the model has been compared with "real" data obtained during normal operation of the plant, covering a wide range of flue gas flow rate, L/G ratio, SO_2 concentration in flue gas and slurry pH. For these less controlled conditions (difficulty to obtain a true steady state), the deviation is less than 5 %.

The desulfurization degrees predicted by the model are sufficiently closed to measured data to consider the model robust and accurate in a broad range of operating and inlet parameters, validating the modeling of the numerous phenomena encountered in FGD and their coupling.

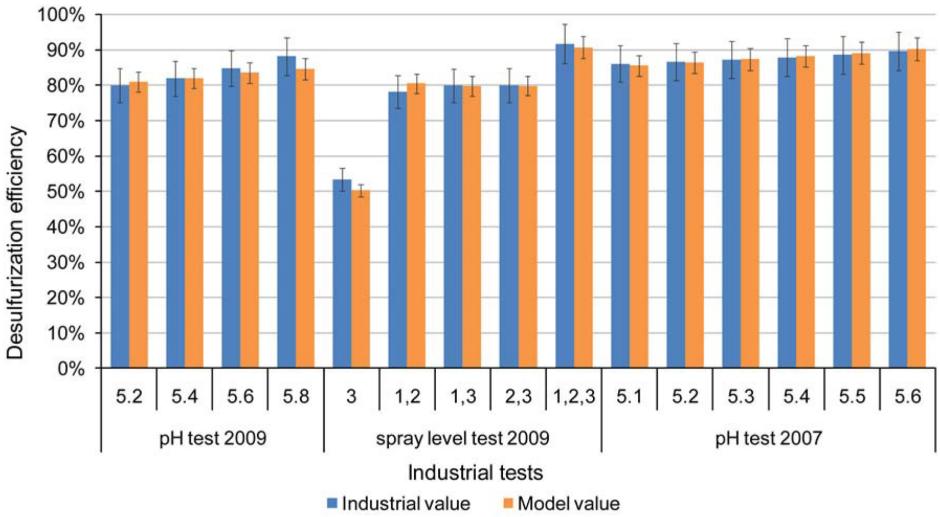

Figure 2. Comparison between model and industrial data for pH and L/G (spray levels) controlled tests on a 600 MW FGD unit (air-fired) [2]

3.2. Case study of a 30 MW_{th} wet FGD unit in oxy-combustion conditions

A more specific validation of the model in oxy-combustion condition can be performed thanks to the data obtained at the 30 MW_{th} oxy-combustion pilot plant operated in Schwarze Pumpe [1]. The wet FGD unit tested was designed to treat flue gas with high SO_2 concentration (up to 11 500 mg/Nm^3, dry) with a large amount of water vapor (around 30 $\%_{vol}$) due to the combustion of lignite and warm recycle, operating at 70 °C.

The experimental results can be compared with simulations obtained with the oxyFGD model. An approximate design based on public information [1,8,9] is used in the model. However, some elements are unknown (e.g. exact liquid flow rates and spray level heights, droplet Sauter mean diameter) and fixed to estimated values. Furthermore, the model cannot currently model tray in absorption tower. Consequently, a rigorous validation cannot be performed but the trends and order of magnitude are compared.

The impact of slurry pH on SO_2 removal efficiency has been experimented in Schwarze Pumpe, showing a removal efficiency increase from 92 to 99.5 % while increasing the slurry pH from 5.2 to 6.1 [9]. Simulations performed in similar conditions (inlet and approximate design without tray) shows an increase from 88 to 99 %. The impact of slurry recirculation flow rate is also simulated as studied in Schwarze Pumpe. Simulations show a decrease of removal efficiency from 97 to 75 % for a flow rate decrease from 100 to 50 % without any tray, where a decrease from 99 to 91 % for 1 tray and from 99 to 94 % for 2 trays was obtained on pilot plant [9]. The addition of trays significantly improve the removal efficiencies, hence the lower values obtained by simulations compared with measurements on the pilot plant.

Furthermore, it has been observed by simulation that the gypsum has higher purity in oxy-combustion conditions (around 98.5 %, depending on pH) than in air-firing (around 95-97 %).

Considering the fact that the exact conditions (inlets, operating parameters and design) are not reported in literature and that our current model cannot simulate operation with trays, the case study of such unit cannot be more conclusive. However, the model is still consistent in trends and sensitivity with respect to main process parameters.

4. Full-scale process analysis

Using this new model, a complete parametric study has been performed for several inlet conditions (different coals, cold/warm recycle, air infiltration) and key operating parameters (L/G ratio, spray levels, slurry pH) in order to evaluate and optimize the process performances such as the removal efficiency, the gypsum quality or economics (CAPEX and OPEX).

Two bituminous coals have been chosen, one with low sulfur content and one with higher sulfur content. The former is the Douglas premium coal suggested by the European Benchmarking Task Force (EBTF), which has a total sulfur content of 0.52 $\%_{wet}$ (0.57 $\%_{dry}$) and the latter is the Pittsburgh No. 8 coal exhibiting a sulfur content of 2.36 $\%_{wet}$ (2.42 $\%_{dry}$).

4.1. Design and performance evaluation

In this paper, the purpose is to evaluate the performance of wet FGD and not to perform a detailed engineering study; simple design rules have therefore been adopted to size FGD, mostly using similitude with air-fired unit [10].

The column is designed using the flue gas flow rate at full-load for oxy-combustion operation. The column diameter is calculated this flow rate to have a gas velocity around 2.5 m/s and the size of the flue gas inlet to have a gas velocity around 6 m/s. The height of the spray levels are fixed by user. The volume of the reaction tank is calculated using the kinetics of limestone dissolution, sulfite oxidation and gypsum precipitation. An estimation of kinetics for the expected performance is calculated and the volume of the reaction tank is calculated using the most limiting reaction (limestone dissolution in almost every case). The Sauter mean diameter of the droplets has been taken equal to 2 mm, the same value used for the modeling of air-firing FGD.

The performance criteria retained for this study are firstly the obtained concentration: degree of desulfurization, CO_2 balance and gypsum purity. Secondly, the energetic performance is looked into, considering the required work for recirculation pumps and air compressor. The liquid is transported from absorber holdup and oxidation tank through gravity flow, the recirculation pumps have therefore to overcome the spray level height and the oxidation tank height. The air compressor has to overcome the water height in the reaction tank. Lastly, the economic aspects are investigated, for a given separation performance and gypsum quality, considering CAPEX (column, pumps, tanks, silo, grinding mill, compressor, filters, hydrocyclones), O&M and OPEX (electricity, limestone, gypsum selling).

Following assumptions have been chosen for FGD process design:

- Absorber and oxidation reactor materials: carbon steel with 50 mm rubber lining,
- All other equipment materials: stainless steel,
- Redundancy strategy: 5x25 % pumps, 8x15 % air compressors, 8x15 % centrifuges.

Regarding techno-economic evaluation, the following hypotheses have been adopted:

- Currency is € of 2011 and the project start up in 2015,
- Base load plant (8700 h/y) with 90 % availability,
- 40 year plant lifetime with 8 % levelization rate and no escalation,
- For investment, equipment cost have been estimated with correlation and a factorial costing method,
- Final investment (TASC) includes engineering, contingencies, owner's, and financial costs,
- For O&M: maintenance 3 %/y, electricity price: 70 €/MWh, limestone price: 16 €/t, no gypsum sales income.

4.2. Results of parametric study

4.2.1. Overall findings

The effect of suspension equilibrium temperature is more limited than it can appear in the Schwarze Pump pilot plant. Indeed, the suspension temperature is mainly driven by the flue gases water content, this water content being influenced by coal moisture and the adopted recycle strategy. With bituminous coal and cold recycle scheme, the flue gas being recycled in the boiler has a water content of approximately 1.5 % before dilution with the dry oxygen. Consequently, consequently the flue gas water content is in the range 12-14 %, not significantly higher than in air-fired cases leading to a suspension temperature around 50 °C. With the same coal and a warm recycle process, this temperature increases to 57 °C due to a flue gas water content of 17 % (see figure 3).

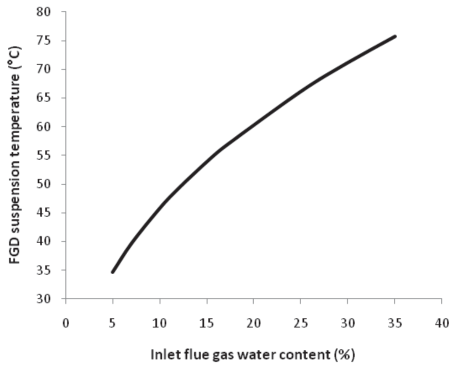

Figure 3: FGD suspension temperature with respect to the inlet water content

As observed on Schwarze Pumpe pilot plant, the gypsum quality seems higher when operating FGD with oxy-combustion flue gases. In all simulations, even with a pH of 6, gypsum has purity above 97.5 %, good enough for sales. Therefore, the optimal operating pH could be increase from the 5.4 to 5.8 range (for air-fired plant) to 5.8 to 6.1 range in oxy-combustion plant.

In oxy-combustion power plant, the flue gas flow rate is reduced by 30 to 50 % consequently the SO_X concentration is increase significantly and the FGD operating and design parameters need to be adapted. In addition, the flue gas needs to be deeply desulfurized before entering the CPU. In order to do so, a second column operating with caustic soda, the Direct Contact Cooled and Polishing Scrubber (DCCPS), is added after the FGD. The target SO_X concentration at the FGD outlet needs to be optimized in order to reduce the overall FGD+DCCPS operating cost. Two SO_2 outlet concentrations are studied: 200 mg/Nm^3 (a similar target than in air-fired plant) and 20 mg/Nm^3 (a desired target to reduce caustic soda consumption and DCCPS effluent production by a factor of 10).

4.2.2. Comparison between low and high sulfur coal in cold recycle process

Due to the significant effect of the pH on the L/G ratio allowing the achievement of a target SO_2 outlet concentration, an operating pH of 5.8 has been chosen but 6.1 can be also considered as acceptable. This ensures high SO_2 removal and satisfactory gypsum quality with some operating margin. Outlet SO_2 concentration as a function of L/G and pH is presented in figure 4.

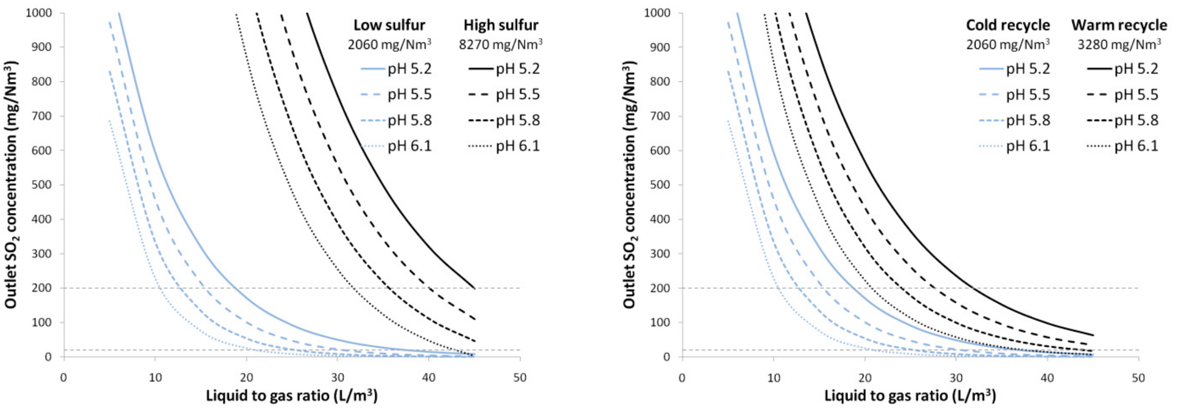

Figure 4: Effect of the L/G and pH on the outlet SO_2 concentration (left: low and high sulfur coals for cold recycle, right: cold and warm recycle for low sulfur coal)

In order to achieve 200 mg/Nm^3 of SO_2 outlet concentration, for a low sulfur coal (2000 mg/Nm^3 in the flue gas), a L/G ratio of 13 L/Nm^3 is needed which is very similar to the same case for air-fired plant (corresponding to a coal with 1 $\%_{wet}$ sulfur). Regarding cost, an investment of approximately 100 M€ is expected for the oxy-combustion case, 34 % less than for an air-fired case of the same net power output [10]; the levelized operating cost (LOC) is around 15 M€/y for both oxy- and air-fired cases. The investment decrease is especially due to the reduction from 2 absorbers of 15 m diameter to 1 absorber of 17 m diameter. For the high sulfur case (8000 mg/Nm^3), a L/G ratio of 35 L/Nm^3 is needed to achieve the same target SO_2 outlet concentration. For this configuration, an investment of 170 M€ is expected with a LOC of 30 M€/y.

Extension of the height of the highest spray banks from 5 m to 10 m seems interesting as it reduce from 13 to 8 L/Nm^3 the L/G for the low sulfur case and from 35 to 18 L/Nm^3 for the high sulfur case. It reduces by 5 % the investment cost for the high sulfur case and the LOC reduce by 16 % of but it has no significant effect on the investment cost for the low sulfur case (competition between the higher column height compensated by lower number of circulating pumps).

Reducing the SO_2 outlet concentration induces an increase of the needed L/G by a factor of 2 (from 13 to 26 L/Nm^3) in the case of a low sulfur coal. For the high sulfur coal, the same trend is observed, the needed L/G increases by 40 % (from 35 to 48 L/Nm^3). The FGD plant cost increase, for reducing the SO_2 outlet concentration from 200 to 20 mg/Nm^3, is +5 % for low sulfur coal and +10 % for high sulfur coal. Finally, increasing suspension pH from 5.8 to 6.1 allows the reduction of L/G by around 5 L/Nm^3 for the same target performances.

4.2.3. Comparison between warm and cold recycle process with low sulfur coal

Warm recycle is an interesting option for increasing the oxy-combustion power plant efficiency. This option changes significantly the flue gases flow rate, water and SO_2 contents. As a consequence, the FGD process needs to be designed for this specific condition. Due to reduction of flue gas treated in the FGD, SO_2 accumulates in the boiler, thus increasing the flue gas SO_2 concentration from 2060 to 3280 mg/Nm^3 for the same coal.

In order to achieve 200 mg/Nm^3 of outlet SO_2 concentration a L/G of 24 L/Nm^3 is necessary. It increases to 41 L/Nm^3 if the target is reduced to 20 mg/Nm^3.

The investment cost is reduced to 75 M€ (25 % decrease compared to cold recycle case) especially due to the reduction of the flue gas flow rate impacting the absorber section (from 17 to 13 m) and the flue gas fan. The LOC is approximately 11 M€/y. Increasing the column height has no significant effect on the investment cost and the LOC.

4.2.4. Effect of air ingress for a low sulfur coal and warm recycle

Air ingress flow has been varied between 1 to 5 % air ingress in the previously studied warm recycle case in order to investigate its influence on FGD performance and optimal design. This induces a change in flue gas flow rate, changing slightly the flue gas velocity in the column and increasing the SO_2 inlet concentration from 3115 to 3469 mg/Nm^3. The desulfurization efficiency is not significantly affected with less than 5 % difference on outlet SO_2 concentration for the same operating condition. The air ingress has a very significant impact on CPU operation and will be tightly monitored for this reason; consequently it is not likely that air ingress will have significant effect on the FGD design.

5. Conclusions

This work focuses on the prediction the wet FGD performances for a full-scale coal fired power plant (1 GW_e) operating in oxy-combustion conditions. A previous model developed for air-fired coal power plant has been adapted to be suited for oxy-combustion flue gas specifications. A thorough investigation of the wet FGD capability when operating under oxy-combustion conditions is proposed. The process design and operating parameters are determined to optimally achieve process performances (energetic, economics).

In contrast with the Schwarze Pump pilot plant operation results, the suspension temperature is not significantly higher than in air-fired combustion. Indeed, the suspension temperature is mainly driven by the flue gases water content. For a bituminous coal and cold recycle process, the flue gas being recycled in the boiler has a water content of approximately 1.5 % and the resulting flue gas water content at FGD inlet is 12 %, leading to a 50 °C temperature suspension.

Regarding projected industrial size FGD for oxy-combustion, there is no significant difficulty to achieve targeted performances. A conservative SO_2 outlet of 200 mg/Nm^3 can be achieve easily both for low and high sulfur coal with L/G in the same range than in air-fired case (13 and 35 L/Nm^3). A more challenging target of 20 mg/Nm^3 could improved the overall oxy-combustion process, this target can be achieve with larger L/G, respectively 26 and 48 L/Nm^3 for low and high sulfur coal with minimal impact of the investment cost. Warm recycle increases the oxy-combustion power plant efficiency, reduces the flue gas to be treated and increases the SO_2 content by 60 %. To cope with this increase inlet SO_2, the L/G ratio is increased by 80 %; but the investment cost is reduced by 25 % compared with cold recycle. Increasing the height of spray banks seems very interesting for high sulfur case as it significantly reduces both investment and operational cost. It has been checked that air ingress have no significant impact on the FGD performances. Finally, a global design of the FGD + DCCPS equipment is needed in order to achieve optimal performance of the flue gas desulfurization at reasonable cost.

6. References

[1] Faber et al. (2011), "Flue gas desulphurization for hot recycle Oxyfuel combustion: Experiences from the 30 MW_{th} Oxyfuel pilot plant in Schwarze Pumpe", Int. J. greenh. Gas Con., vol. 5(S1), pp. S210-S223.

[2] Neveux and Le Moullec (2011), "Wet Industrial Flue Gas Desulfurization Unit: Model Development and Validation on Industrial Data", Ind. Eng. Chem. Res., vol. 50, pp. 7579-7592.

[3] Hansen et al. (2011), " Performance of a Wet Flue Gas Desulfurization Pilot Plant under Oxy-Fuel Conditions", Ind. Eng. Chem. Res., vol. 50, pp. 4238-4244.

[4] Pinsent et al. (1956). "The Kinetics of Combination of Carbon Dioxide with Hydroxide Ions." Trans. Faraday Soc., vol. 52, pp. 1512-1520.

[5] Jian-song et al. (2007). "Oxidation inhibition of sulfite in dual alkali flue gas desulfurization system". J. Environ. Sci., 19, 226–231.

[5] Zhang and Lu (2013). "Study on Kinetic Parameters and Reductive Decomposition Characteristics of FGD Gypsum", Cleaner Combustion and Sustainable World, pp 411-417.

[6] Xiang et al. (2009)."Dissolution rate of limestone for wet flue gas desulfurization in the presence of sulfite", J. Hazard. Mat., 168, 1059–1064

[7] Brewer (1982). "Thermodynamic Values for Desulfurization Processes". ACS Symposium Series 188; American Chemical Society. Washington, DC, 1982.

[8] Burchhardt et al. (2011), "Flue Gas Desulphurisation for Hot Recycle Oxyfuel Combustion: Experiences from the 30 MW_{th} Oxyfuel Pilot Plant in Scwharze Pumpe", The 2rd Oxyfuel Combustion Conference (PCCC2), Queensland, Australia, September 12-16 2011.

[9] Yan et al. (2013), "Performance and System Optimisation of Flue Gas Desulphurisation for Oxy-coal Combustion", The 3rd Oxyfuel Combustion Conference (OCC3), Ponferrada, Spain, September 9-13 2013.

[10] Gansely (2008), "Wet FGD System Overview and Operation", WPCA Wet FGD Seminar, Power Gen International, December 1, 2008.