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A simple realistic modeling of full-scale wet limestone FGD units

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ABSTRACT

A model of wet limestone flue gas desulfurization (WLFGD) system has been developed based on the use of the number of transfer units (NTU) and height of transfer unit (HTU) focused to full-scale coal-fired power plants. The model describes the process occurring in the absorber as the most important step in the WLFGD system by establishing what increase in SO_2 removal can be achieved as the higher levels of nozzles come progressively into service when initially the first spray header is operating alone, and keeping the other operating conditions under control. This relative improvement of the SO_2 removal can be obtained from only one datum: the number of mass transfer units when only the first spray level is on service (N_1). The model computes the gains in both the volumetric overall mass transfer coefficient and the number of transfer units. The model can be used to evaluate data or changes in an existing full-scale system as well as to evaluate proposed system designs and even as a pre-design tool in relation to the number of spray levels on service under controlled operating conditions. The model is tested on the basis of some data taken from a power plant and from the literature. The model results agree well with the real and published data.

1. Introduction

Nowadays, different desulfurization technologies are available to control SO_2 emission in coal-fired power stations. The most widespread is wet limestone flue gas desulfurization (WLFGD), which has undergone considerable development over the past 30 years in terms of SO_2 removal, efficiency, reliability, and costs. Limestone is generally quite a bit cheaper than lime, making it more popular for large FGD systems. Therefore, wet scrubbers, especially wet limestone desulfurization scrubbers, are the front-running FGD technologies [1,2].

In this process, the flue gas is treated with limestone (calcium carbonate) slurry normally in a spray column. Limestone is mixed with water in a slurry supply tank. The fresh limestone slurry is fed to the absorber sump. The limestone/gypsum slurry is pumped from the absorber sump (holding tank) up to the horizontal spray headers at different levels at the top of the scrubber. Normally, the number of spray levels varies from 4 to 6. The spray header pumps operate in an on/off mode, i.e., there is no flow control on the headers, which is the most usual operation mode in full-scale WLFGD plants. Uniformity of spray, small drop size with high velocity and low energy of atomization are the desired criteria for the atomizer [3]. The main design parameters related to the spray header performance are the droplet size and velocity that are function of the atomizing pressure and the liquid flow rate in the nozzles. As the slurry falls down the tower, it meets the rising flue gas and reacts with the SO_2 in the flue gas. A large contact area between the slurry and the flue gas is established and SO_2 is absorbed. The removal of SO_2 occurs at temperatures between 45 and 60 °C. Then, the slurry drops to the slurry tank after reacting with the flue gas. Calcium sulfite and bisulfite ($CaSO_3$ and $Ca(HSO_3)_2$) are formed in the chemical reactions that occur in the scrubber. The absorber sump (liquor or liquid phase) is agitated and aerated (forced-oxidation mode) to produce gypsum or calcium sulfate dihydrate ($CaSO_4{\cdot}2H_2O$) salts that are removed as sludge. This sludge, extracted from the absorber sump, is thickened, dewatered, and washed for subsequent storage before dispatch from the site (Fig. 1). Normally, the byproduct gypsum can be sold rather than incurring a disposal cost, which includes a landfill tax; this solution also lessens the environmental impact. The final product is calcium sulfate dihydrate (gypsum), and the limestone content cannot exceed 3–4 wt% limestone in solids, according to most worldwide standards, to be saleable [4]. There are many important parameters affecting the design and operation of a FGD scrubber although the most relevant are the liquid-to-gas ratio, the reaction tank pH, the absorber gas velocity, the reagent utilization and the oxidation fraction.

Even though the overall reaction is simple, the chemistry of the process is quite complex. Many researchers have studied and modeled these complex processes under typical desulfurization conditions. The models include sub-models for the four rate-

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Nomenclature

E	enhancement factor in chemical absorption (–)
f_r	reduction factor for α_i-coefficients (–)
G	superficial molar gas flow rate (kmol/(h m^2))
L/G	liquid-to-gas ratio (L/Nm^3)
HTU	height of a transfer unit (m)
(K_Ga)	volumetric overall mass transfer coefficient (kmol/(h m^3 bar)) when only SL$_1$ is on service for the entire scrubber
$(K_Ga)'$	volumetric overall mass transfer coefficient (kmol/(h m^3 bar)) when SL$_1$ and SL$_2$ are on service for the entire scrubber
$(K_Ga)''$	volumetric overall mass transfer coefficient (kmol/(h m^3 bar)) when SL$_1$, SL$_2$ and SL$_3$ are on service for the entire scrubber
$(K_Ga)'''$	volumetric overall mass transfer coefficient (kmol/(h m^3 bar)) when SL$_1$, SL$_2$, SL$_3$ and SL$_4$ are on service for the entire scrubber
$(K_Ga)_i$	volumetric overall mass transfer coefficient (kmol/(h m^3 bar)) for SL$_i$ when there are not upper spray levels on service
$(K_Ga)'_i$	volumetric overall mass transfer coefficient (kmol/(h m^3 bar)) for SL$_i$ zone when only the just upper spray level is on service apart from that all the lower ones
$(K_Ga)''_i$	volumetric overall mass transfer coefficient (kmol/(h m^3 bar)) for SL$_i$ zone when the just two upper spray levels are on service apart from that all the lower ones
$(K_Ga)'''_i$	volumetric overall mass transfer coefficient (kmol/(h m^3 bar)) for SL$_i$ zone when the three upper spray levels are on service apart from that all the lower ones
NTU	number of mass transfer units (–)
N_1	number of mass transfer units when only the first spray level is on service (–)
P	pressure inside the spray absorber (bar)
y_i	SO$_2$ molar fraction after passing through the SL$_i$ (mol/mol) and upper spray levels are off service
y'_i	SO$_2$ molar fraction after passing through the SL$_i$ (mol/mol) and only the just upper spray level is on service, apart from all lower ones
y''_i	SO$_2$ molar fraction after passing through the SL$_i$ (mol/mol) and the just two upper spray levels are on service, apart from all lower ones
y'''_i	SO$_2$ molar fraction after passing through the SL$_i$ (mol/mol) and the just three upper spray levels are on service, apart from all lower ones
z	physical/geometrical height (m)
z^e	effective height for mass transfer (m)

Greek symbols

α_i	multiplier factor in which $(K_Ga)_1$ increases in SL$_1$ due to SL$_i$ when this spray level comes into service (–)
ηSL_i	desulfurization efficiency achieved in SL$_i$ (–)
ΔN_i	NTU increase in SL$_1$ due to the upper spray level SL$_i$ (–)

Subscripts

in	absorber inlet
out	absorber outlet
0	relative to SO$_2$ molar fraction if no increase in (K_Ga) is considered when more spray levels come into service

influencing steps: absorption of sulfur dioxide, oxidation of $SO_3{}^{2-}$, dissolution of limestone, and crystallization of gypsum. Complexity and level of detail of the models differ somewhat, but they all estimate the overall SO$_2$ removal efficiency [5].

Apart from the mathematical models featured to chemical aspects, now CFD code allows to deal with the gas and slurry flow patterns, which normally have been assumed to be simplified ones [6].

Despite intensive modeling work, industrial equipment is mostly designed by scale-up of process data obtained in pilot plants, thus illustrating the difficulty in the application of these models to the full-scale plants. The complex chemistry and the simultaneous mass and heat transfer involved in the wet limestone desulfurization process is not an easy task, so solving the set of equations is very time-consuming not only for a dynamic model but also even for the steady-state case. Therefore, a simple model based on easy global concept would be useful to chemical engineers for who to continuously solve the rigorous model may be impractical; thus, it may be welcome to consider a realistic approach when dealing with a model of a WLFGD unit in a full-scale plant.

This paper does not try to develop a detailed model but a simple and directly applicable model to full-scale plants, and thus, the aim of the present work is to describe a realistic model that can be used as a tool for the analysis of the WLFGD spray-units in full-scale coal-fired power plants.

2. General outline of the model

The most important process in the WLFGD system is the absorption of sulfur dioxide. Sulfur dioxide is absorbed in the spray absorption zone by reacting with the limestone slurry drops, so the chemical absorption in the absorber is the most complicated and significant step in scrubber. In this modeling work, limestone dissolution, crystallization of gypsum are under control by closing control loops that manipulate fresh limestone slurry, make-up water flow rate, agitation and sludge flow rate controlling thus the holding tank level and pH. Furthermore, sulfite oxidation, which is of fundamental importance in WLFGD process, will be under controlled conditions by manipulating the air flow rate entered to the holding tank, and the sulfite oxidation rate has been assumed to be a fixed rate independent of the sulfite concentration. Therefore, the absorbent dissolution and oxidation and crystallization that occur in the slurry zone will not be considered in the approach of this work, and thus a model describing the process in the absorber is the focus of this paper.

According to Brogren and Karlsson [7] and Yeh and Rochelle [8], and by analyzing the SO$_2$ removal process using the two-film theory of mass-transfer, droplets exiting the spray nozzles lead to a negligible mass transfer resistance on the liquid side, making the limestone/gypsum slurry close to the nozzles along the spray headers most effective in SO$_2$ removal. This is due to the sheet formed just in the nozzle outlet and the internal turbulence of the liquid phase once sprayed, which decreases as the droplets fall through the tower. As the exposure time or the partial pressure of SO$_2$ increases the gas-side resistance decreases. Therefore, far from the spray nozzles the liquid-side resistance should be considered. In any case, when more spray headers come into service the SO$_2$ concentration tends to be lower and the gas-side resistance gains

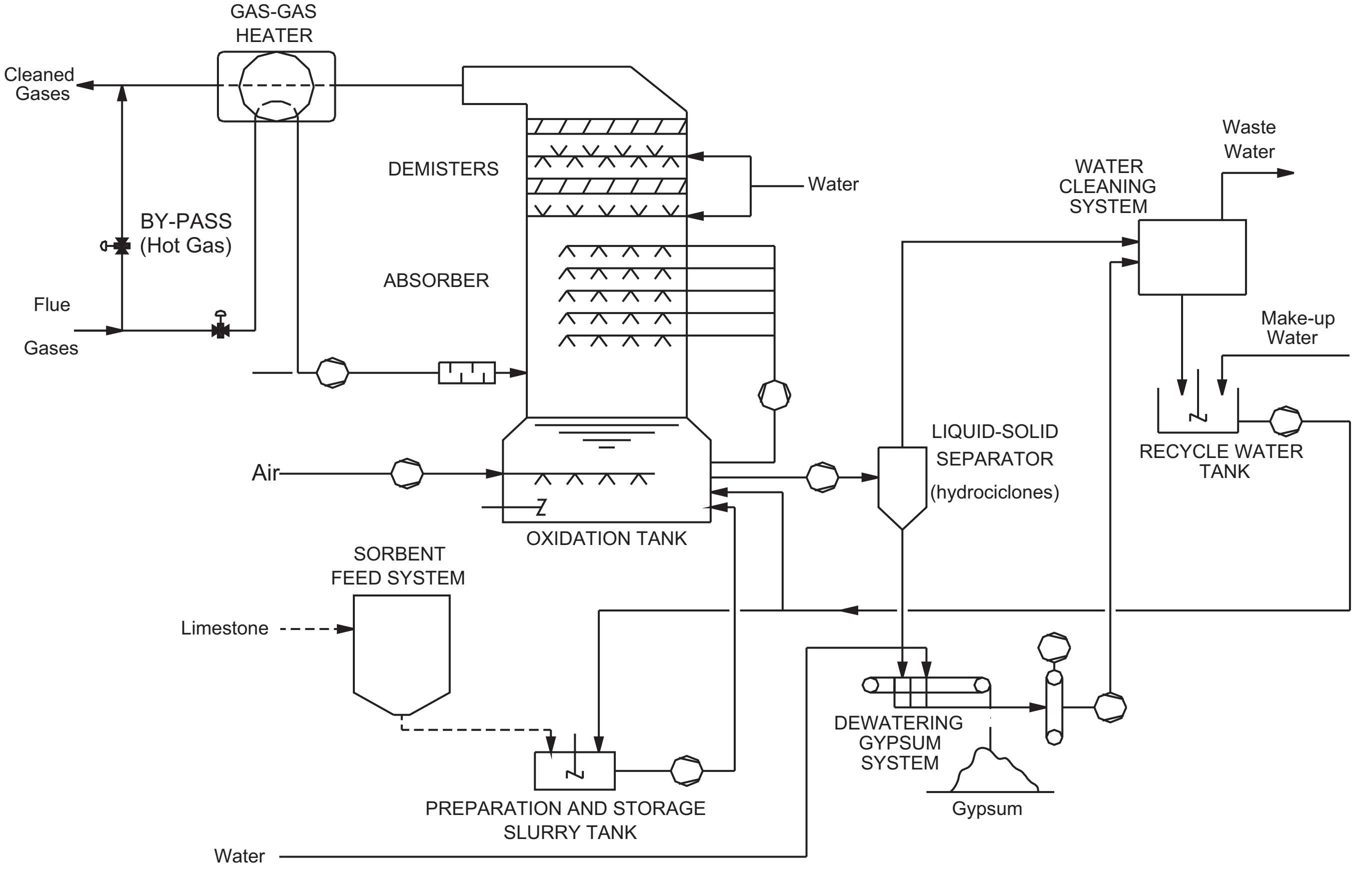

Fig. 1. Wet limestone desulfurization basic diagram (forced-oxidation mode).

importance with regard to the liquid-side resistance, especially in the top spray headers.

Pasiuk-Bronikowska et al. [9] reported that when the concentration of sulfur dioxide is less than 0.2% in volume and the absorbent used is alkaline, the main resistance to mass transfer occurs within the gas phase. When the concentration of sulfur dioxide is greater than 0.2% in volume, the liquid-side resistance to mass transfer should be taken into account. This corresponds to coal with a sulfur content higher than 2.5 wt%.

In this paper, it is assumed that the effective contact takes place within a small space under the spray levels and the highest mass-transfer rates occurs near the nozzles, so the residual capacity of slurry to further SO_2 removal is neglected against to that initial in the zone between two consecutive spray levels but considered again when reaching the zone close to nozzle located in lower spray headers. This is equivalent to use an overall gas-side resistance where the driving force can be approached to the partial pressure of SO_2 in the gas side assuming a very low SO_2 concentration inside the sheet/droplet far from the liquid film, i.e., the pressure corresponding to the liquid concentration in the bulk of liquid considered as liquid concentration in equilibrium is much lower than that corresponding to the liquid concentration in equilibrium just in the interface, as given by Henry's law. Therefore, the number of transfer units is obtained within a zone near the slurry atomization in the nozzles. On the other hand, it is obvious that for a given superficial molar gas flow-rate (kmol/(h m^2)), a higher slurry liquid-to-gas ratio or L/G ratio (litres of slurry/Nm^3 of gas) involves a higher superficial molar liquid flow-rate, so the contact area increases when more spray headers come into service.

The model assumes a steady state operation of the spray column. Likewise, the gas phase concentration is uniformly distributed at the inlet and outlet of the column and all droplets have the same concentration when exiting the nozzles for all the spray headers. The flow of gas and droplets is regarded as plug flow with negligible gas phase back-mixing. There are not significant differences in the SO_2 concentration as a function of distance to the wall, so an average SO_2 concentration will be used in each cross-section. Also, heats of reaction and dissolution are neglected and the system is isothermal. With regard to the nozzles and droplets, a good atomizer that produces a fairly uniform spray with droplet diameters small enough to generate large interfacial area of contact but large enough to prevent excessive entrainment is assumed. There is an insignificant wall effect for the liquid phase, and internal circulation and oscillation of the droplets are not considered, although both of them increase the mass-transfer rate compared to diffusion alone. Indeed, for a droplet size higher than 1 mm the mass transfer is higher due probably to oscillation or turbulent circulation.

3. Model development

This section describes the model development of the absorber using the transfer unit approach. The first step is to provide a preliminary and extremely simple model where two additional simplifications are considered:

- With any upper spray level coming into service the contacting area linearly increases, in such a way that, e.g., three spray levels lead to an available contact area three-times higher than when only the lowest spray level is on service.
- Every spray level is only effective (i.e., the slurry is active) in the space just below. Thus, the mass transfer occurs mainly within a

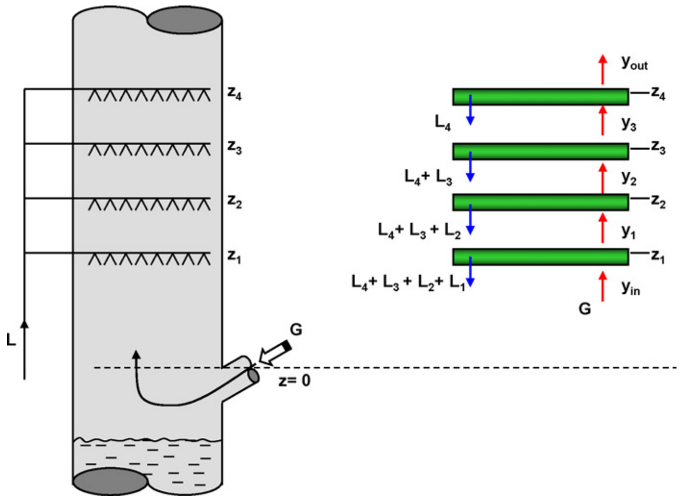

Fig. 2. A scheme of the absorber to modeling the SO_2 removal.

region close to nozzles and below of it the mass transfer almost not happens.

The slurry is injected into the absorber over several spray levels, each one with an own recirculation pump. Each spray bank is provided with numerous spray nozzles for a proper atomization of the slurry. The spray levels will be named as SL_1, SL_2, SL_3 and SL_4 and so on from the bottom up. The model is based on the use of height of mass transfer unit (HTU), which includes the volumetric overall mass transfer coefficient (K_Ga), and the number of mass transfer units (NTU). Fig. 2 illustrates a scheme followed to modeling. As, it is well-known, the total height is the product of HTU and NTU, i.e.:

$$z_T^e = \mathrm{HTU} \times \mathrm{NTU} = \sum_i \mathrm{HTU}_i \times \mathrm{NTU}_i \tag{1a}$$

$$\mathrm{HTU}_i = \frac{G}{(K_Ga)_iP} \therefore \mathrm{NTU}_i = \ln\left(\frac{y_{i-1}}{y_i}\right) \tag{1b}$$

$$\begin{aligned} z_T^e &= z_1^e + z_2^e + z_3^e + z_4^e = \frac{G}{(K_Ga)_1P}\ln\left(\frac{y_{in}}{y_1}\right) + \frac{G}{(K_Ga)_2P}\ln\left(\frac{y_1}{y_2}\right) \\ &\quad + \frac{G}{(K_Ga)_3P}\ln\left(\frac{y_2}{y_3}\right) + \frac{G}{(K_Ga)_4P}\ln\left(\frac{y_3}{y_{out}}\right) \\ &= \frac{G}{(K_Ga)P}\sum_{i=1}^{4}\ln\left(\frac{y_{i-1}}{y_i}\right) \quad z_i^e < z_i \end{aligned} \tag{2}$$

In Eqs. (1a) and (2) the partial heights (z_i^e) do not correspond to geometrical or physical heights (z_i), i.e., not all the physical space between spray headers is useful for mass transfer.

In this model, the volumetric overall mass transfer coefficient, (K_Ga), always keeps constant by assuming that each spray header has the same number of nozzles and that every nozzle provides the same slurry flow rate with the same droplet distribution size. Therefore, it is being assumed that droplets leaving the nozzles in a given spray header are ineffective in the zone corresponding to the lower spray levels.

As shown Gerbec et al. [10], Warych et al. [11,12] and Zhong et al. [13], by their models and experimental results, when the flue gas flow rate is that of the design value, desulfurization efficiency increases exponentially with the increase of L/G ratio. Thus, (K_Ga) experimentally increases with L/G ratio but the simple model above described assumes the same value of (K_Ga) through the tower. Therefore, the model could be improved if a fraction of slurry droplets falling from the upper headers also contributes to the SO_2 removal when passing through the lower headers. Then, in Eq. (2):

$$(K_Ga)_1 > (K_Ga)_2 > (K_Ga)_3 > (K_Ga)_4$$

Thus, $(K_Ga)_4$ is equivalent to the previous value of (K_Ga) in Eq. (2). When a new spray level comes into service the height and the contact area become higher. Between the upper spray header (SL_4) and the immediately inferior one (SL_3) the contacting area will be lower than below this, because the total area is now increased with the area of the droplets from the upper header. However, not all the droplets (and hence, the relative contact area) can be considered as effective since they arrive to the just inferior partially saturated of absorbed SO_2. Furthermore, the enhancement factor of chemical absorption will be also lower, as explained later. Therefore, the volumetric overall mass transfer coefficient's increase will not be twice from SL_4 and SL_3 but less.

Then, for each spray level the following equations can be obtained (the derivation of these relationships is described in Appendix A):

Spray level 1:

$$\mathrm{HTU} \times \mathrm{NTU} = H_1 \times N_1 = \frac{G}{(K_Ga)_1P} \times \ln\left(\frac{y_{in}}{y_1}\right) \tag{3}$$

Spray level 2:

$$\frac{G}{(K_Ga)'P} \times \ln\left(\frac{y_{in}}{y_2}\right) = \frac{GN_1}{(K_Ga)_1P} \times \left(1 + \frac{1}{\alpha_1}\right) + \frac{G}{(K_Ga)_1P} \times \left(\frac{\Delta N_2}{\alpha_1}\right) \tag{4}$$

Spray level 3:

$$\begin{aligned} \frac{G}{(K_Ga)''P} \times \ln\left(\frac{y_{in}}{y_3}\right) &= \frac{GN_1}{(K_Ga)_1P} \times \left(1 + \frac{1}{\alpha_1} + \frac{1}{\alpha_1\alpha_2}\right) + \frac{G}{(K_Ga)_1P} \\ &\quad \times \left(\frac{\Delta N_2 + \Delta N_3}{\alpha_1\alpha_2} + \frac{\Delta N_2}{\alpha_1}\right) \end{aligned} \tag{5}$$

Spray level 4:

$$\begin{aligned} &\frac{G}{(K_Ga)'''P} \times \ln\left(\frac{y_{in}}{y_{out}}\right) \\ &= \frac{GN_1}{(K_Ga)_1P} \times \left(1 + \frac{1}{\alpha_1} + \frac{1}{\alpha_1\alpha_2} + \frac{1}{\alpha_1\alpha_2\alpha_3}\right) + \frac{G}{(K_Ga)_1P} \\ &\times \left(\frac{\Delta N_2 + \Delta N_3 + \Delta N_4}{\alpha_1\alpha_2\alpha_3} + \frac{\Delta N_2 + \Delta N_3}{\alpha_1\alpha_2} + \frac{\Delta N_2}{\alpha_1}\right) \end{aligned} \tag{6}$$

Thus, it can be obtained the differential contribution of each spray level with respect to the just inferior one:

$$\mathrm{SL1\,(reference)}: \frac{GN_1}{(K_Ga)_1P}$$

$$\mathrm{SL2} - \mathrm{SL1}: \frac{GN_1}{(K_Ga)_1P} \times \frac{1}{\alpha_1} + \frac{G}{(K_Ga)_1P} \times \left(\frac{\Delta N_2}{\alpha_1}\right)$$

$$\mathrm{SL3} - \mathrm{SL2}: \frac{GN_1}{(K_Ga)_1P} \times \frac{1}{\alpha_1\alpha_2} + \frac{G}{(K_Ga)_1P} \times \left(\frac{\Delta N_2 + \Delta N_3}{\alpha_1\alpha_2}\right)$$

$$\begin{aligned} \mathrm{SL4} - \mathrm{SL3}: &\frac{GN_1}{(K_Ga)_1P} \times \frac{1}{\alpha_1\alpha_2\alpha_3} + \frac{G}{(K_Ga)_1P} \\ &\times \left(\frac{\Delta N_2 + \Delta N_3 + \Delta N_4}{\alpha_1\alpha_2\alpha_3}\right) \end{aligned}$$

Two terms characterize these relationships, relative to the SL_1 contribution (and lower spray levels if this is the case):

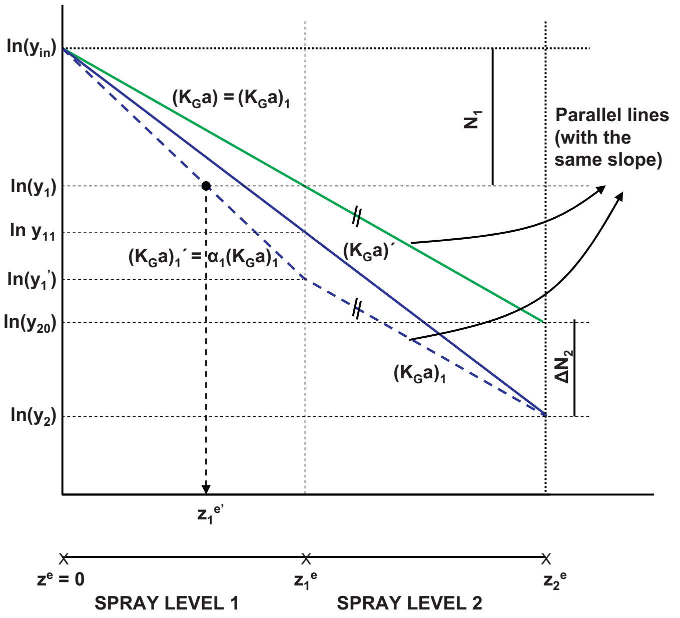

Fig. 3. A graphical approach to modeling when the second spray level comes into service.

1st term N_1 value (number of mass transfer obtained in the first spray level, when there are not other nozzles on service), and (K_Ga) that increases in such a way that, when spray level 2 comes into service then $(K_Ga)'_1 = \alpha_1(K_Ga)_1$, thus decreasing HTU (height of a transfer unit when the first spray level is only on service). This is extrapolated to the other cases: $(K_Ga)''_1 = \alpha_1\alpha_2(K_Ga)_1$ and $(K_Ga)'''_1 = \alpha_1\alpha_2\alpha_3(K_Ga)_1$, relative to the just inferior spray level.

2nd term $(K_Ga)_1$ is kept constant as well as HTU, and the number of mass transfer units is increased as $\Delta N_2/\alpha_1$, $(\Delta N_2 + \Delta N_3)/\alpha_1\alpha_2$ and $(\Delta N_2 + \Delta N_3 + \Delta N_4)/\alpha_1\alpha_2\alpha_3$, relative to the just inferior spray level, as SL_2, SL_3 and SL_4 come progressively into service.

Now, the α_i-coefficients can be related with N_1 and ΔN_i, as well as with primed (K_Ga) to (K_Ga) ratio. In effect, Eqs. (3)–(6) suggest the use of a graphical representation as that illustrated in Fig. 3 that allows to interpret how the model works. From this figure, which depicts the results of the two first spray level when the second one comes into service, some other useful relationships can be obtained (their derivation is described in Appendix B):

$$z_1^e = \frac{GN_1}{(K_Ga)_1 P} \therefore z_1^{e'} = \frac{GN_1}{\alpha_1 (K_Ga)_1 P} \Rightarrow z_1{}^{e'} = \frac{z_1^e}{\alpha_1} \tag{7}$$

$$\Delta N_2 = \ln\left(\frac{y_1}{y_2}\right) - N_1 \tag{8}$$

$$\alpha_1 = \frac{\ln(y_1/y_2)}{N_1} = 1 + \frac{\Delta N_2}{N_1} \tag{9}$$

$$\frac{(K_Ga)'}{(K_Ga)'_1} = \frac{1+\alpha_1}{2\alpha_1} \tag{10}$$

The primed variable refers to a modified value regarding with that obtained by the initial model. The subscript ‘0’ for the SO_2 molar fraction in the gas phase refers to a value obtained by using that initial model.

In case of using more spray headers, the following expressions are achieved:

Spray levels on-service: 1 + 2 + 3:

$$\Delta N_3 = \ln\left(\frac{y_2}{y_3}\right) - \ln\left(\frac{y_1}{y_2}\right) \tag{11}$$

$$\alpha_2 = 1 + \frac{\Delta N_3}{N_1 + \Delta N_2} \tag{12}$$

$$\frac{(K_Ga)''}{(K_Ga)''_1} = \frac{1+\alpha_1+\alpha_1\alpha_2}{3\alpha_1\alpha_2} \tag{13}$$

Spray levels on-service: 1 + 2 + 3 + 4:

$$\Delta N_4 = \ln\left(\frac{y_3}{y_{out}}\right) - \ln\left(\frac{y_2}{y_3}\right) \tag{14}$$

$$\alpha_3 = 1 + \frac{\Delta N_4}{N_1 + \Delta N_2 + \Delta N_3} \tag{15}$$

$$\frac{(K_Ga)'''}{(K_Ga)'''_1} = \frac{1+\alpha_1+\alpha_1\alpha_2+\alpha_1\alpha_2\alpha_3}{4\alpha_1\alpha_2\alpha_3} \tag{16}$$

It can be observed that from measurable values (SO_2 concentrations at the outlet of each spray level) the parameters α_i, ΔN_i and primed (K_Ga) to (K_Ga) ratio may be determined.

The derivation of these expressions is obtained in a similar way that for SL_1 and SL_2 (Appendix B). Fig. 4 depicts the meaning of the modeling in a graphical way for all spray headers, where it is exhibited the contribution of each spray header zone as more spray header pumps come into service. This plot provides an illustrative global description of the model. Solid lines link the natural logarithm (LN) of SO_2 inlet concentration to LN of SO_2 outlet concentration when several levels are on service and dashed lines show the LN of SO_2 concentration at intermediate locations for each spray header. It can be observed how the slope of lines is proportional to (K_Ga) of each spray level as well as the increase in the number of mass transfer units as more spray levels come into service. Likewise, according to the model, some lines are parallel each other as illustrated by small marks drawn on lines.

Therefore, it can be observed that the model provides the relative improvement achievable when the spray headers over the first one come progressively into service with respect to the SO_2 removal in the WFGD unit operating only with the first spray header. Therefore, the reference of the model is the number of mass unit transfer when only the first spray header is on service, N_1. Some pilot plant tests or even full-scale tests could be also carried out in order to approximate the N_1-value. Anyway, it must be noted that the aim of this study is to obtain the relative enhancement aforementioned, so this is the main novelty.

Thus, the next step is to estimate the value for the parameters of the model, i.e., α_i and ΔN_i (and, hence, primed (K_Ga) to (K_Ga) ratio) only depending on N_1, so no measured SO_2 concentrations would have to be previously obtained. When the second spray level (SL_2) comes into service, it behaves like SL_1 operating alone, but the liquid leaving SL_2 is partially saturated of SO_2 when reaching the lower spray level, so the available calcium is now lower. Consequently, the residual slurry can go on absorbing SO_2 but its absorption capacity is reduced. This reduction can be quantified taking a basis of 1 (for a given calcium-to-sulfur ratio and a slurry pH) for SL_1 or the upper spray level on service, as a reference value of usefulness. Thus, the effectiveness of the slurry from SL_2 in the SL_1 zone close to nozzles, that contributes as ΔN_2, is reduced by the desulfurization efficiency achieved in SL_2 (η_{SL_2}), i.e., the relative value will not be 1 but $(1 - \eta_{SL_2})$. Therefore:

$$\begin{aligned} &\frac{\Delta N_2}{N_1} = (1-\eta_{SL_2}) = \left(1 - \frac{y_{in}-y_1}{y_{in}}\right) = \frac{y_1}{y_{in}} = e^{-N_1} \Rightarrow \Delta N_2 \\ &\Delta N_2 = N_1 e^{-N_1} \end{aligned} \tag{17}$$

Thus, according to Eq. (9):

$$\alpha_1 = 1 + (1-\eta_{SL_2}) = 1 + e^{-N_1} \tag{18}$$

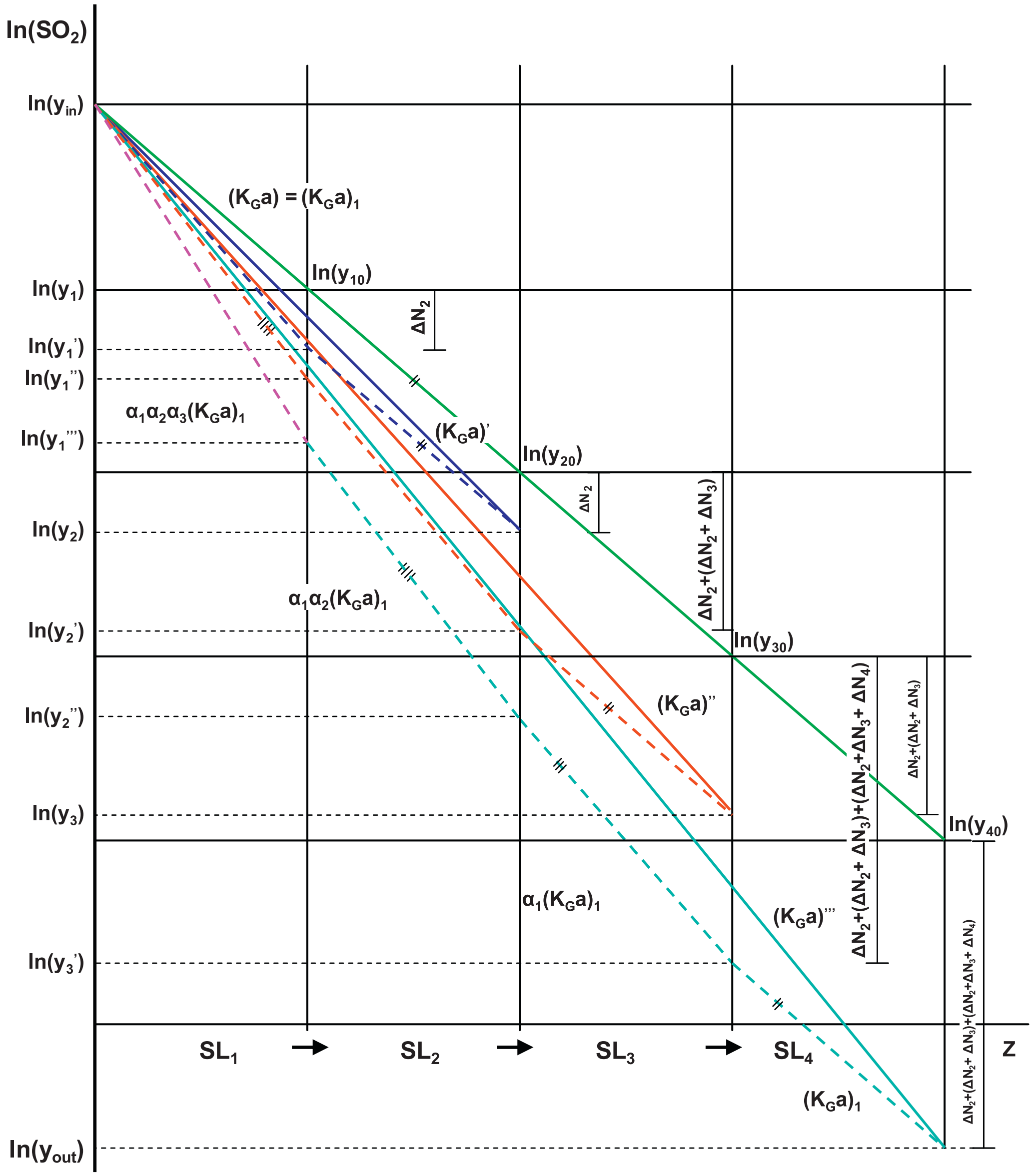

Fig. 4. A graphical meaning of the modeling showing the effect of every spray header (small marks on lines denote parallel lines each other depending on the number of marks).

And, likewise, from Eq. (10):

$$\frac{(K_Ga)'}{(K_Ga)'_1} = \frac{1+\alpha_1}{2\alpha_1} = \frac{2+e^{-N_1}}{2(1+e^{-N_1})} \tag{19}$$

The procedure can be extended to the other parameters regarding with the upper spray headers, and for absorbers with various spray levels, the following general expressions could be used (Appendix C):

$$\Delta N_k = \Delta N_{k-1} \exp\left(-\left(N_1 + \sum_{i=2}^{k-1} \Delta N_i\right)\right)$$
$$= N_1 e^{-N_1} \exp\left(-\sum_{j=2}^{k-1}\left(N_1 + \sum_{i=2}^{j} \Delta N_i\right)\right) \quad (k \geq 3) \tag{20}$$

$$\alpha_k = 1 + \frac{e^{-N_1} \exp\left(-\sum_{j=2}^{k}\left(N_1 + \sum_{i=2}^{j} \Delta N_i\right)\right)}{1 + e^{-N_1} + \sum_{z=2}^{k-1} e^{-N_1} \exp\left(-\sum_{j=2}^{z}\left(N_1 + \sum_{i=2}^{j} \Delta N_i\right)\right)} \quad (k \geq 3) \tag{21}$$

In fact and as previously anticipated, the estimation obtained for α_1, and hence for the other α_i-coefficients, must be still lower because the liquid alkalinity's decrease and the sulfite concentration's increase in the liquid as SO_2 is absorbed lead to a reduction of the enhancement factor (E) relative to chemical absorption. The spray tower operates with high E only close to the nozzle, but decreases very quickly due to pH drop, and hence the major part of the absorber operates with E-values of 4–8. Brogren and Karlsson [7] estimated an E-value around 15 for the first spray level. Since the main difference between overall resistance close to nozzles from

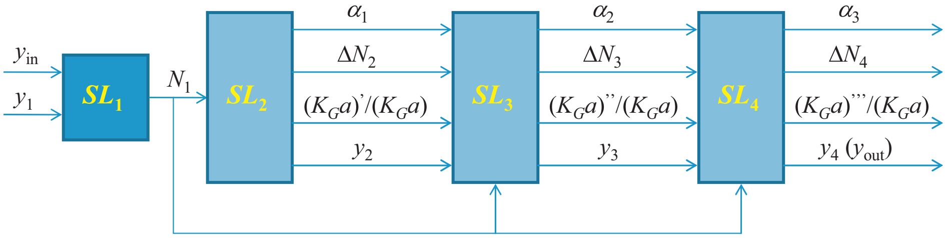

Fig. 5. Flow-chart of the model.

that far enough from the header is just in the *E*-factor and besides the gas-film resistance is quite low in the droplets zone just below the first spray header [7], it is postulated a reduction factor (f_r) to apply to α_i-coefficients of around 0.4 (6/15). On the other hand, DeVincentis [14] estimated the number of transfer units values of 1–3 from full-scale data for SO_2 absorption in limestone slurry, but only 0.5–1.0 of those transfer units are expected in a spray may be due to the spray itself [8]. Then, new limits of 0.5 and 0.3 for the reduction factor are proposed for α_i-coefficients, so the following interval can be used for α_1:

$$[1+0.3e^{-N_1},\ 1+0.5e^{-N_1}]$$

Anyway, the reduction factor for α_i-coefficients has an empirical nature so the proposed values for f_r must be taken into account as tentative values.

Fig. 5 illustrates a simplified flow-chart where the input data and the output results of the model are shown.

4. Model validation

The methodology suggested in this paper to carry out the tests necessary to verify the model in a power plant consists of keeping constant the main operating parameters, except the number of recycle pumps, i.e., the inlet SO_2 concentration as well as flue gas flow-rate must be kept constant; the pH is set and controlled by manipulating the limestone slurry flow-rate (once fixed limestone concentration or slurry density) and, thus, the limestone/gypsum slurry flow-rate (and hence, the L/G ratio) is the variable manipulated to achieve a wished SO_2 removal. This operation mode may be performed in any power plant, so the tests carried out may be planned as follows: first only the SL_1 is on service and, by measuring SO_2 concentrations at the inlet and outlet of the spray contactor, N_1 is determined. Likewise, $(K_Ga)_1$ may also be estimated by using mass transfer correlations. Then, SL_2 is on service so $(K_Ga)'$ can be obtained, and so on with the upper spray header, SL_3 and SL_4, thus determining $(K_Ga)''$ and $(K_Ga)'''$. All α_i and ΔN_i are also obtained. Apart from the SO_2 concentration at the inlet and outlet of the unit, other data that should be recorded are the number of spray level on service, the flue gas flow rate, the pH of the reaction/holding tank, the temperature profile through the tower and the limestone consumption. Other parameters that usually are taken in a discontinuous way are the gypsum/limestone slurry density and fresh limestone slurry density. The operating conditions during the test must have a steady behaviour through the time in which the test is carried out, so it is necessary to close the control loops. This set of tests should be mainly repeated for several pH set points and different boiler loads. Obviously, if the coal is changed the model should be re-calibrated.

Anyway, taking into account the relative characteristic of the proposed model as referred to N_1 and $(K_Ga)_1$ when only SL_1 is operating, the differences obtained operating under other values of pH, boiler load and coal will not be likely too significant. The differences will be probably in N_1 and $(K_Ga)_1$ values for these cases.

Table 1
Process conditions in the Spanish WFGD unit.

Description	Values	Units
Inlet SO_2 concentration	1650	ppmv
Gas temperature at the absorber inlet	100	°C
Holding tank pH	4.8	–
Flue gas flow rate	900000	Nm^3/h
Limestone slurry density	1.28	kg/l

To validate the model of the spray absorber process, it is necessary to have real data from operation of wet FGD unit. Experiments can be performed in pilot plants but special care must be taken since the scrubbers are narrower and the droplets after a very short path may collide with the absorber wall beneath the nozzle. In full-scale FGD scrubbers in coal-fired power plants only a small fraction of the liquid feed collides with the wall. However, detailed information about absorber design, flue gas flow rate and liquid-to-gas ratio and other real operation parameters is lacking in many publications and real data from operation almost always are missing thus making difficult to find enough data to validate modeling SO_2 removal in full-scale WLFGD units. The model has been tested on the basis of data taken from a full-scale WLFGD unit located in a Spanish power station and from the literature.

In a power station located at the North of Spain, some tests have been carried out in a spray column of 14.5 m of internal diameter and almost 24 m of effective height. In this unit the liquid level of the holding tank and the first spray level (SL_1) are located at 9.5 and 15.8 m from the base, respectively. The other three nozzles headers are spaced 1.35 m each other. The distance between the gas entrance and SL_1 is 3.5 m. The total number of nozzles is 464 distributed through four spray levels. Each nozzle has a capacity of 63.6 m^3/h at 48.3 kPa, and the average drop diameter is 1.67 mm.

Table 1 shows the process conditions for one of the tests carried out in the Spanish WFGD unit. Table 2 contains the results from this test. It can be observed how by putting more spray headers into service, the L/G ratio increase leads to higher desulfurization efficiency. At the same time, the pressure drop increases from 27.3 to 56.7 mm w.c. and the limestone consumption also raises from 2.47 to 6.84 t/h.

Fig. 6 depicts the average SO_2 concentration measured at the absorber outlet (left ordinates axis) as well as the NTU (N_1, ΔN_2, ΔN_3 and ΔN_4) values measured and calculated by model

Table 2
Results from one of the tests carried out in the Spanish WFGD unit.

Description	Spray headers pumps on-service			
	1	1 + 2	1 + 2 + 3	1 + 2 + 3 + 4
Outlet SO_2 concentration (ppmv)	964	438	201	92
Pressure drop in the column (mm w.c.)	27.3	35.9	46.7	56.7
Gas temperature at the absorber outlet (°C)	47.3	46.7	46.7	46.9
Limestone consumption (t/h)	2.47	3.75	4.91	6.84

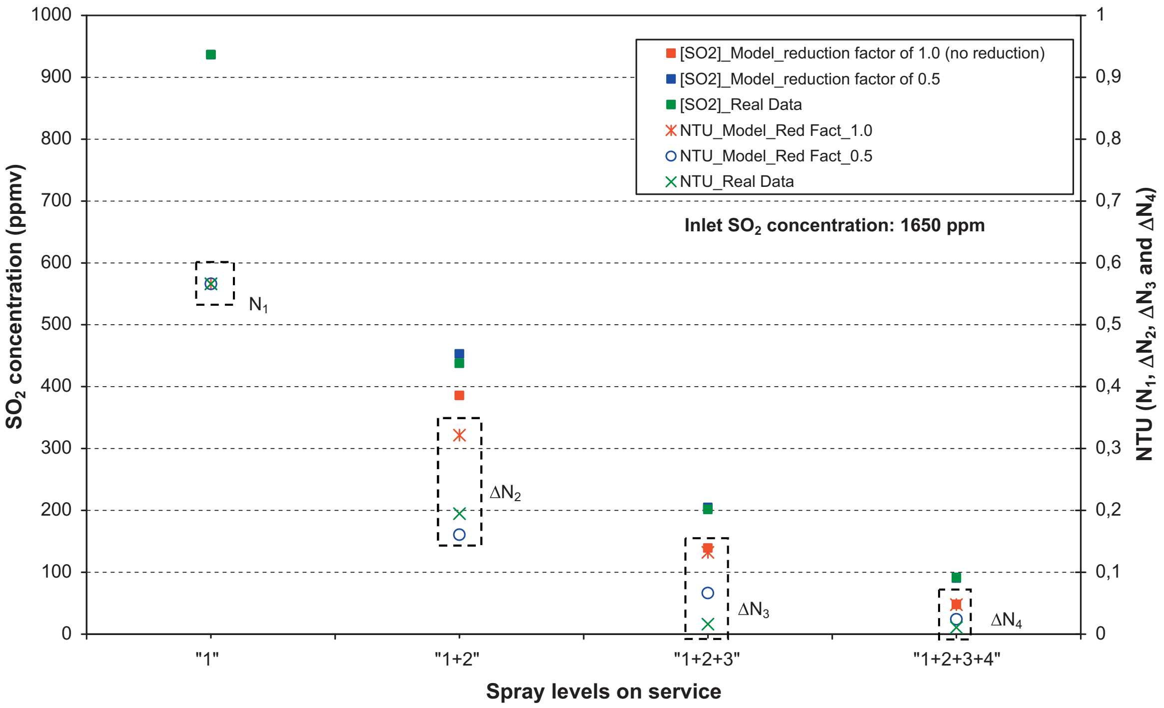

Fig. 6. Results from the Spanish WFGD unit.

(right ordinates axis) versus spray levels on service or L/G ratio (abscissas axis) by changing the gypsum/limestone slurry flowrate. It can be observed that, by selecting a reduction factor of 0.5 for α_i-coefficients, the modeled and full-scale data matches very well.

On the other hand, data from the 300-MWe power station in the USA [15] have been used. In this plant, the SHU technology is tested, where there is a first co-current section and a second counter-current section. This latter consists of spray nozzles at three levels to complete SO_2 absorption, previously started in a co-current section. This SHU configuration is not a problem for testing the model proposed in this paper since the two sections of the absorber are disengaged with regard to the chemical absorption, and the same configuration for the co-current section has been selected. In effect, the data taken from this plant correspond to those obtained by keeping constant the number of spray headers of the co-current section on service as well as the other operating conditions. During the tests, the pH was 4.1 ± 0.1 despite changing SO_2 removals that occurred when test conditions were changed, thanks to the pH control loop.

The test plan was designed to study the effect of recycle slurry liquid-to-gas ratio (L/G) by varying the number of spray header

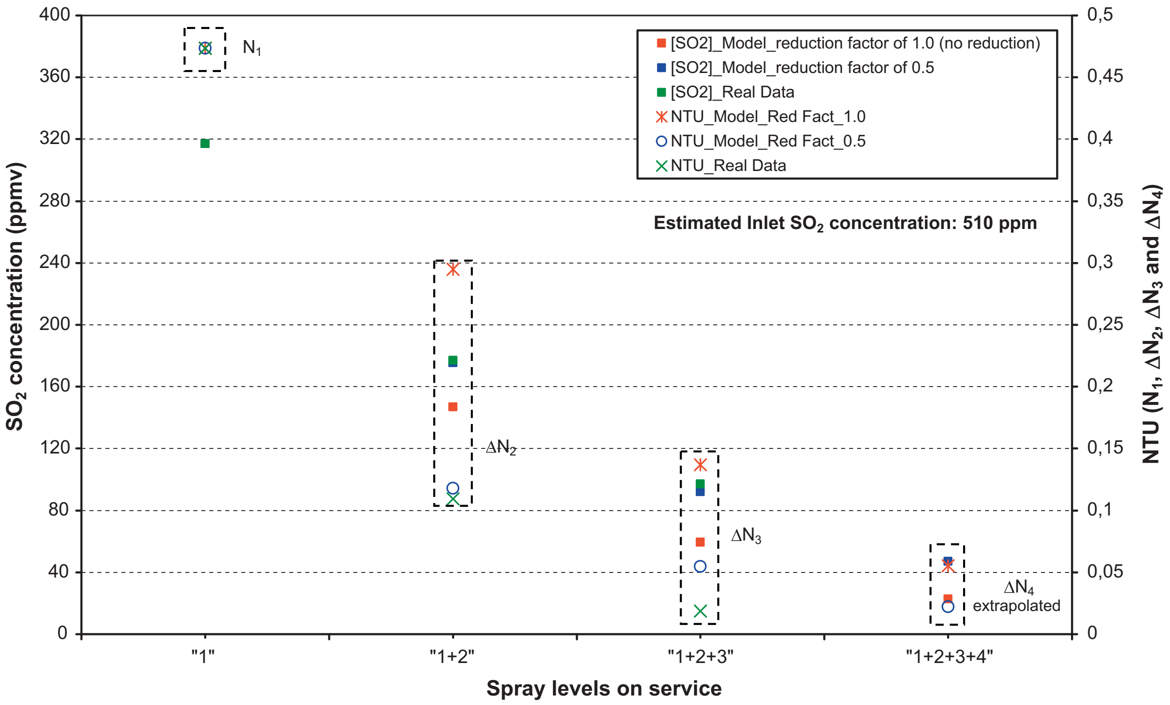

Fig. 7. Results from the American WFGD unit [15].

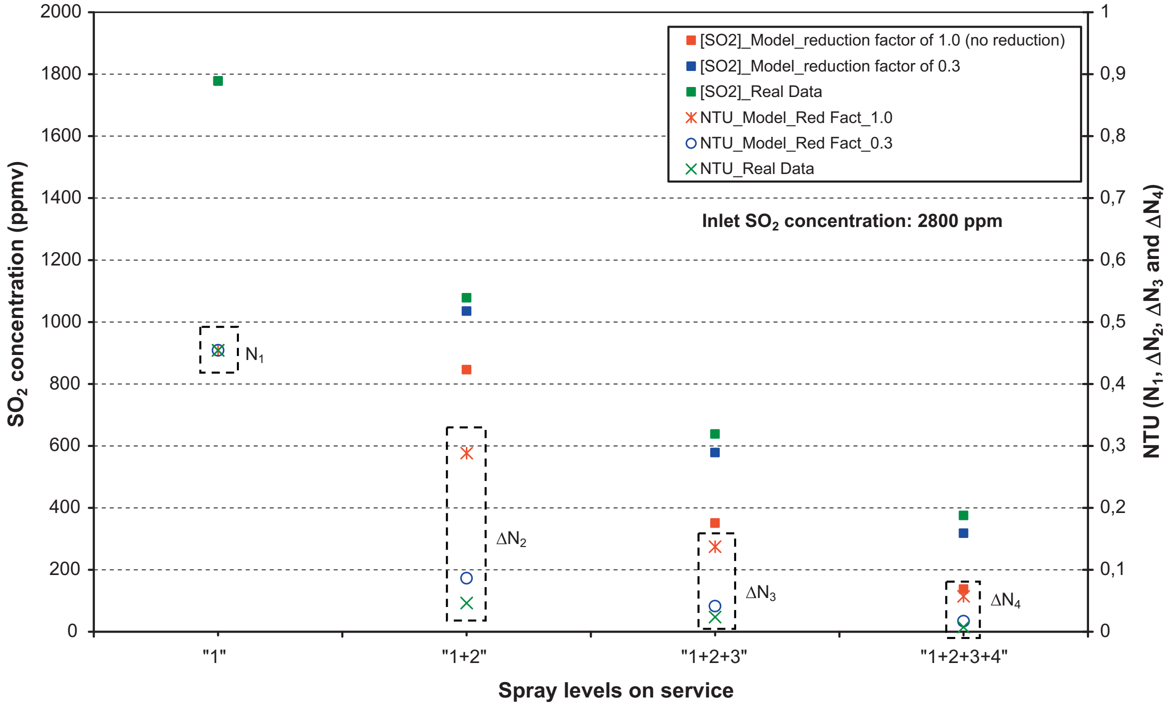

Fig. 8. Results from the Gerbec et al. study [10] (pH of 5).

pumps in operation, and it was obtained that the SO$_2$ removal varied depending upon which counter-current spray headers were in use. Thus, Fig. 7 depicts a given case, where the plant was operating with the entire co-current absorption section on service. In this figure, it can be observed the average SO$_2$ outlet concentration as well as N_1 and ΔN_i when header pumps on service are progressively increased from the first one to the third one. Likewise, it is shown the results obtained by the model in relative terms for a reduction factor of 0.5 and with no reduction for α_i-coefficients. The agreement between the experimental and modeled results is very high. Values for a hypothetical new spray level just upper the third one are extrapolated and given.

Gerbec et al. [10] verified their model using data from a pilot plant located at Slovenian power plant, with a capacity of 17000 m^3/h of flue gas, an absorber tower equipped with six levels of nozzles, internal diameter of 1.3 m and useful height of 12 m. In Figs. 8–10, a comparison of the model now proposed and the results obtained by Gerbec et al at three pH values (5.0, 5.5 and 5.7) and for the first four spray levels by changing the L/G ratio is shown, including both the SO$_2$ concentration and N_1 and ΔN_i, under the

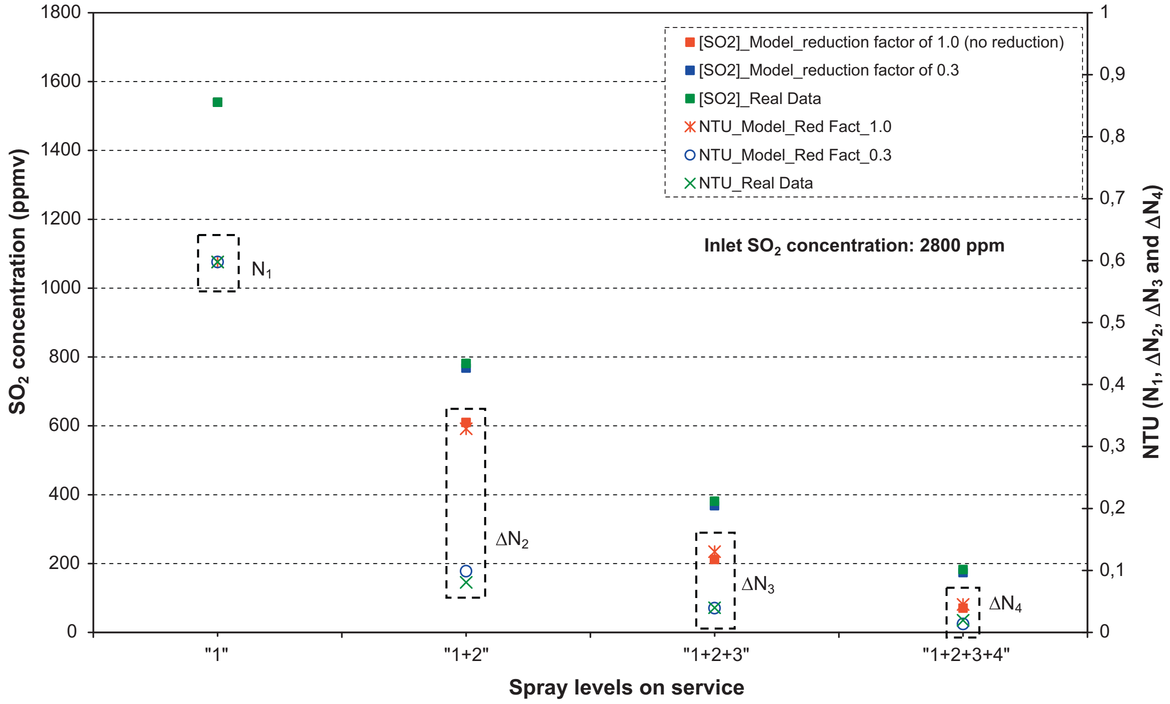

Fig. 9. Results from the Gerbec et al. study [10] (pH of 5.5).

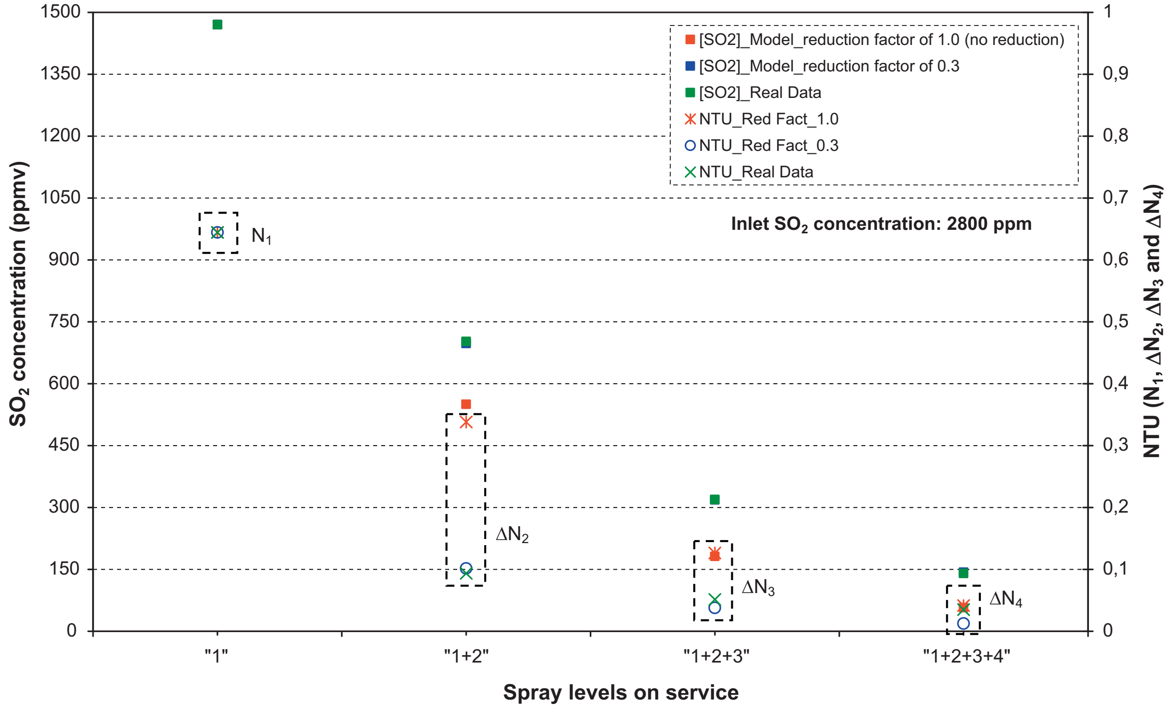

Fig. 10. Results from the Gerbec et al. study [10] (pH of 5.7).

following conditions: flue gas flow rate of 10000 m^3/h, inlet SO_2 concentration of 2800 ppmv. The modeled data results, using a factor of 0.3 for α_i-coefficients fits very well the real data obtained in that paper for all cases.

Finally, Duo et al. [16] carried out experiments in a pilot plant with a spraying absorber of 0.5 m diameter and 1.20 m in height and holding tank. Some data of this paper have been taken to provide an additional reference to compare with results from the proposed model. Fig. 11 shows, once again, the real data (those from the paper mentioned) and the modeled results. By selecting a reduction factor of 0.3 for α_i-coefficients, real data agrees well with the results from the model. Note the small scale of the unit tested, so the model may be also used for pilot plants.

From the available data, a possible error range of the model has been analyzed by taking from the α_1-interval above proposed the value farthest from that better fitting the model results to the real data. In terms of the increase in SO_2 removal efficiency, from SL_1 to $SL_1 + SL_2$ the biggest model error is about 6 to 14% and when the fourth spray level is put on service the biggest model error is about 4 to 11% (from $SL_1 + SL_2 + SL_3$ to $SL_1 + SL_2 + SL_3 + SL_4$). The biggest

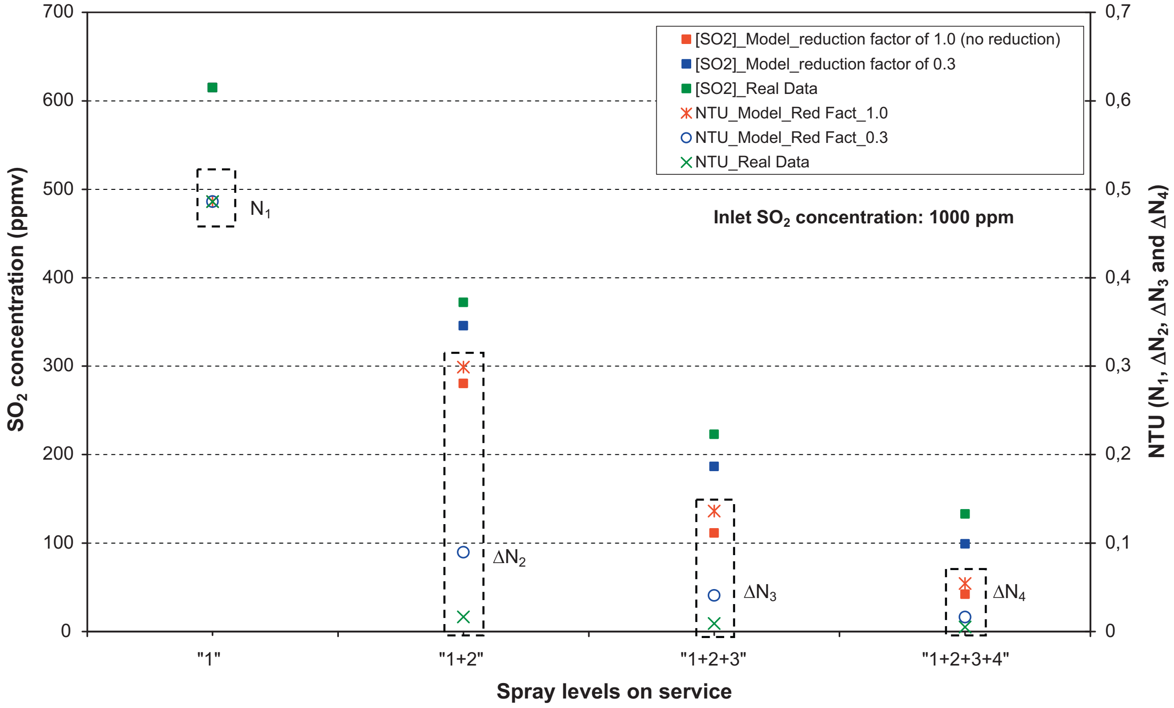

Fig. 11. Results from the Duo et al. study [16].

total error for the SO_2 removal efficiency from only SL_1 on service to all the four spray headers on service ($SL_1 + SL_2 + SL_3 + SL_4$) is about 3–9%. If the best α_1-value is taken from the cited α_1-interval then the error range is quite reduced and the upper range limit of the model error is about 6% although it is normally lower than 4%. Taking into account the simplicity of the model, these results may be considered as reasonably good.

5. Conclusions

A model of wet limestone flue gas desulfurization (WLFGD) has been proposed to predict how much the SO_2 removal increases as more spray headers are on service in relation to the removal obtained when the unique spray level on service is the lowest one, under the same operating conditions: flue gas flow-rate, pH holding tank, inlet SO_2 concentration, pressure and temperature inside the absorber. Only the L/G ratio varies by manipulating the recycled slurry to the tower, and the control loops are closed. The model gives a relationship between (K_Ga) and L/G ratio in such a way that each new upper spray header behaves as the just lower, and the lower ones increase their partial efficiency, i.e., the number of mass transfer units. The model computes the gains in both the volumetric overall mass transfer coefficient and the number of transfer units. In order to explain the meaning of the model, the increase in both HTU and NTU is divided in two terms for each spray level that comes into service taking the just lower spray level contribution as a reference: the one that keeps constant the NTU value of the just lower spray level and reduces HTU (increases K_Ga); the other one keeps constant HTU (and K_Ga) and increases NTU. Expressions have been obtained for each spray level, so multiplier factors, α_i-coefficients, the increase in NTU (ΔN_i) and primed (K_Ga) to (K_Ga) ratio are computed. These parameters as well as the relative improvement of the SO_2 removal can be obtained from only one datum: the number of mass transfer units when only the first spray level is on service (N_1).

The result is the following for a spray tower with four spray levels:

$$z_T^e = z_1^e + z_2^e + z_3^e + z_4^e = \frac{G}{P} \times N_1 \times \frac{1}{(K_Ga)_1} \times \left(1 + \frac{1}{\alpha_1} + \frac{1}{\alpha_1\alpha_2} + \frac{1}{\alpha_1\alpha_2\alpha_3}\right) + \frac{G}{(K_Ga)_1P} \times \left(\frac{\Delta N_2}{\alpha_1} + \frac{\Delta N_2 + \Delta N_3}{\alpha_1\alpha_2} + \frac{\Delta N_2 + \Delta N_3 + \Delta N_4}{\alpha_1\alpha_2\alpha_3}\right)$$

In this equation, Z_i^e represents the zone effective for mass transfer, which is just the zone close to nozzle in each spray header. Thus, Z_i^e is lower than space between spray headers. Likewise, a reduction factor for α_i-coefficients that takes into account a decrease in the enhancement factor is provided within an interval, but noting its empirical nature. It must be remarked the graphical chart (Fig. 4) proposed that allows to summarize the contribution of each spray level and gives a realistic description of the model by plotting natural logarithms of SO_2 molar fraction versus spray levels on service.

To verify the model some full-scale data from power plants and data from the published literature have been used, by figures that illustrate the SO_2 concentration in the gas at the outlet of the spray tower as well as the number of transfer units and its increase, versus the spray levels on service (1, 1 + 2, 1 + 2 + 3, and 1 + 2 + 3 + 4). These figures show that real data matches very well with modeled results, using different reduction factors within the provided interval for α_i-coefficients.

It should be noted that one of the advantages of using NTU and HTU in modeling is that their values can be used to extrapolate tests or operating data on a spray contactor to other systems or conditions. The model can be used to evaluate data or changes in an existing full-scale system as well as to evaluate proposed system designs and even as a pre-design tool in relation to the number of spray levels on service under controlled operating conditions.

Appendix A.

In this annex, the derivations of the relationships obtained for each spray header is described.

Spray level 1:

$$\text{HTU} \times \text{NTU} = H_1 \times N_1 = \frac{G}{(K_Ga)_1P} \times \ln\left(\frac{y_{in}}{y_1}\right);$$

$$N_1 = \ln\left(\frac{y_{in}}{y_1}\right)$$

Spray level 2:

$$\begin{aligned}\frac{G}{(K_Ga)'P} \times \ln\left(\frac{y_{in}}{y_2}\right) &= \frac{G}{(K_Ga)'_1P} \times \ln\left(\frac{y_{in}}{y'_1}\right) + \frac{G}{(K_Ga)_2P} \times \ln\left(\frac{y'_1}{y_2}\right)\\ &= \frac{G}{(K_Ga)'_1P} \times \left[\ln\left(\frac{y_{in}}{y_1}\right) + \ln\left(\frac{y_1}{y'_1}\right)\right]\\ &\quad + \frac{G}{(K_Ga)_1P} \times \ln\left(\frac{y'_1}{y_2}\right)\end{aligned}$$

$$(K_Ga)'_1 > (K_Ga)_1 = (K_Ga)_2 \Rightarrow (K_Ga)'_1 = \alpha_1(K_Ga)_1 \therefore \alpha_1 > 1$$

$$\frac{y'_1}{y_2} = \frac{y_{in}}{y_1} \therefore \frac{y_{in}}{y'_1} > \frac{y_{in}}{y_1} \quad (y'_1 < y_1)$$

$$\Delta N_2 = \ln\left(\frac{y_1}{y'_1}\right),$$

$$\begin{aligned}\frac{G}{(K_Ga)'P} \times \ln\left(\frac{y_{in}}{y_2}\right) &= \frac{G}{\alpha_1(K_Ga)_1P}[N_1 + \Delta N_2] + \frac{G}{(K_Ga)_1P} \times N_1\\ &= \frac{GN_1}{(K_Ga)_1P} \times \left(1 + \frac{1}{\alpha_1}\right) + \frac{G}{(K_Ga)_1P} \times \left(\frac{\Delta N_2}{\alpha_1}\right)\end{aligned}$$

For the third and fourth spray levels, the same procedure is followed to obtain the positive contribution of each new spray level with respect to the just inferior and express it by two terms.

Spray level 3:

$$\begin{aligned}\frac{G}{(K_Ga)''P} \times \ln\left(\frac{y_{in}}{y_3}\right) &= \frac{G}{(K_Ga)''_1P} \times \ln\left(\frac{y_{in}}{y''_1}\right) + \frac{G}{(K_Ga)'_2P}\\ &\quad \times \ln\left(\frac{y''_1}{y'_2}\right) + \frac{G}{(K_Ga)_3P} \times \ln\left(\frac{y'_2}{y_3}\right)\end{aligned}$$

$$\begin{aligned}\frac{y_{in}}{y''_1} &= \frac{y_{in}}{y_1} \times \frac{y_1}{y'_1} \times \frac{y'_1}{y''_1} \Rightarrow \ln\left(\frac{y_{in}}{y''_1}\right)\\ &= N_1 + \Delta N_2 + \Delta N_3 \quad (y''_1 < y'_1 < y_1)\end{aligned}$$

$$\Delta N_3 = \ln\left(\frac{y'_1}{y''_1}\right)$$

$$\frac{y''_1}{y'_2} = \frac{y_{in}}{y'_1} = \frac{y_{in}}{y_1} \times \frac{y_1}{y'_1} \Rightarrow \ln\left(\frac{y''_1}{y'_2}\right) = N_1 + \Delta N_2$$

$$\frac{y'_2}{y_3} = \frac{y'_1}{y_2} = \frac{y_{in}}{y_1}$$

$$(K_Ga)_3 = (K_Ga)_2 = (K_Ga)_1$$

$$(K_Ga)'_2 = (K_Ga)'_1 = \alpha_1(K_Ga)_1 \therefore \alpha_1 > 1$$

$$(K_Ga)''_1 = \alpha_2(K_Ga)'_1 = \alpha_2\alpha_1(K_Ga)_1 \therefore \alpha_2 > 1$$

$$\begin{aligned}\frac{G}{(K_Ga)''P}\times\ln\left(\frac{y_{in}}{y_3}\right) &= \frac{G}{\alpha_2\alpha_1(K_Ga)_1P}\times[N_1+\Delta N_2+\Delta N_3]\\ &\quad+\frac{G}{\alpha_1(K_Ga)_1P}\times[N_1+\Delta N_2]+\frac{G}{(K_Ga)_1P}\times N_1\\ &=\frac{GN_1}{(K_Ga)_1P}\times\left(1+\frac{1}{\alpha_1}+\frac{1}{\alpha_1\alpha_2}\right)+\frac{G}{(K_Ga)_1P}\\ &\quad\times\left(\frac{\Delta N_2+\Delta N_3}{\alpha_1\alpha_2}+\frac{\Delta N_2}{\alpha_1}\right)\end{aligned}$$

Spray level 4:

$$\begin{aligned}\frac{G}{(K_Ga)'''P}\times\ln\left(\frac{y_{in}}{y_4}\right) &= \frac{G}{(K_Ga)'''_1P}\times\ln\left(\frac{y_{in}}{y'''_1}\right)+\frac{G}{(K_Ga)''_2P}\\ &\quad\times\ln\left(\frac{y''_1}{y''_2}\right)+\frac{G}{(K_Ga)'_3P}\times\ln\left(\frac{y''_2}{y'_3}\right)\\ &\quad+\frac{G}{(K_Ga)_4P}\times\ln\left(\frac{y'_3}{y_{out}}\right)\end{aligned}$$

$$\begin{aligned}\frac{y_{in}}{y'''_1} &= \frac{y_{in}}{y_1}\times\frac{y_1}{y'_1}\times\frac{y'_1}{y''_1}\times\frac{y''_1}{y'''_1}\Rightarrow\ln\left(\frac{y_{in}}{y'''_1}\right)\\ &= N_1+\Delta N_2+\Delta N_3+\Delta N_4 \quad (y'''_1<y''_1<y'_1<y_1)\end{aligned}$$

$$\Delta N_4=\ln\left(\frac{y''_1}{y'''_1}\right)$$

$$\frac{y'''_1}{y''_2}=\frac{y_{in}}{y''_1}=\frac{y_{in}}{y_1}\times\frac{y_1}{y'_1}\times\frac{y'_1}{y''_1}\Rightarrow\ln\left(\frac{y'''_1}{y''_2}\right)=N_1+\Delta N_2+\Delta N_3$$

$$\frac{y''_2}{y'_3}=\frac{y''_1}{y'_2}=\frac{y_{in}}{y'_1}=\frac{y_{in}}{y_1}\times\frac{y_1}{y'_1}\Rightarrow\ln\left(\frac{y''_2}{y'_3}\right)=N_1+\Delta N_2$$

$$\frac{y'_3}{y_{out}}=\frac{y_{in}}{y_1}$$

$$(K_Ga)_4=(K_Ga)_3=(K_Ga)_2=(K_Ga)_1$$

$$(K_Ga)'_3=(K_Ga)'_2=(K_Ga)'_1=\alpha_1(K_Ga)_1 \therefore \alpha_1>1$$

$$(K_Ga)''_2=(K_Ga)''_1=\alpha_2(K_Ga)'_1=\alpha_2\alpha_1(K_Ga)_1 \therefore \alpha_2>1$$

$$(K_Ga)'''_1=\alpha_3(K_Ga)''_1=\alpha_3\alpha_2(K_Ga)'_1=\alpha_3\alpha_2\alpha_1(K_Ga)_1 \therefore \alpha_3>1$$

$$\begin{aligned}&\frac{G}{(K_Ga)'''P}\times\ln\left(\frac{y_{in}}{y_{out}}\right)\\ &=\frac{G}{\alpha_3\alpha_2\alpha_1(K_Ga)_1P}\times[N_1+\Delta N_2+\Delta N_3+\Delta N_4]\\ &\quad+\frac{G}{\alpha_2\alpha_1(K_Ga)_1P}\times[N_1+\Delta N_2+\Delta N_3]+\frac{G}{\alpha_1(K_Ga)_1P}\\ &\quad\times[N_1+\Delta N_2]+\frac{G}{(K_Ga)_1P}\times N_1\end{aligned}$$

$$\begin{aligned}\frac{G}{(K_Ga)'''P}\times\ln\left(\frac{y_{in}}{y_{out}}\right) &= \frac{GN_1}{(K_Ga)_1P}\times\left(1+\frac{1}{\alpha_1}+\frac{1}{\alpha_1\alpha_2}+\frac{1}{\alpha_1\alpha_2\alpha_3}\right)\\ &\quad+\frac{G}{(K_Ga)_1P}\times\left(\frac{\Delta N_2+\Delta N_3+\Delta N_4}{\alpha_1\alpha_2\alpha_3}\right.\\ &\quad\left.+\frac{\Delta N_2+\Delta N_3}{\alpha_1\alpha_2}+\frac{\Delta N_2}{\alpha_1}\right)\end{aligned}$$

Appendix B.

In this annex, the derivations of the relationships obtained from Fig. 3 are described.

Spray levels: 1 + 2:

$$\frac{N_1+\Delta N_2}{\alpha_1(K_Ga)_1}=\frac{N_1}{(K_Ga)_1}=\frac{\ln(y_{in}/y_{11})}{(K_Ga)'}\Rightarrow\Delta N_2=N_1(\alpha_1-1)$$

$$\ln y_{11}=\frac{\ln y_{in}+\ln y_2}{2}\Rightarrow y_{11}=\sqrt{y_{in}\times y_2}$$

$$\frac{y_1}{y'_1}=\left(\frac{y_{20}}{y_2}\right);\qquad\frac{y_1}{y_{20}}=\frac{y_{in}}{y_1}$$

$$\begin{aligned}\Delta N_2 &= \ln\left(\frac{y_1}{y'_1}\right)=\ln\left(\frac{y_{20}}{y_2}\right)=\ln\left(\frac{y_1^2/y_{in}}{y_2}\right)\\ &=\ln\left(\frac{y_1}{y_2}\right)-\ln\left(\frac{y_{in}}{y_1}\right)\Rightarrow\Delta N_2=\ln\left(\frac{y_1}{y_2}\right)-N_1\end{aligned}$$

$$\begin{aligned}\frac{G}{(K_Ga)'P}\times\ln\left(\frac{y_{in}}{y_2}\right) &= \frac{G}{(K_Ga)'P}\times[2N_1+\Delta N_2]\\ &=\frac{G}{\alpha_1(K_Ga)_1P}[N_1+\Delta N_2]+\frac{G}{(K_Ga)_1P}\times N_1\\ &=\frac{GN_1}{(K_Ga)_1P}\times\left(1+\frac{1}{\alpha_1}\right)+\frac{G}{(K_Ga)_1P}\times\left(\frac{\Delta N_2}{\alpha_1}\right)\end{aligned}$$

$$\frac{[2N_1+\Delta N_2]}{(K_Ga)'}=\frac{[N_1+\Delta N_2]}{\alpha_1(K_Ga)_1}+\frac{N_1}{(K_Ga)_1}$$

$$\frac{(K_Ga)'}{(K_Ga)_1}=\frac{2N_1+\Delta N_2}{\dfrac{N_1+\Delta N_2}{\alpha_1}+N_1}=\frac{2N_1+\Delta N_2}{2N_1}$$

$$\left.\begin{array}{l}\dfrac{(K_Ga)'}{(K_Ga)_1}=\dfrac{N_1(1+\alpha_1)}{2N_1}=\dfrac{1+\alpha_1}{2}\\ \dfrac{(K_Ga)'_1}{(K_Ga)_1}=\alpha_1\end{array}\right\}\Rightarrow\frac{(K_Ga)'}{(K_Ga)'_1}=\frac{1+\alpha_1}{2\alpha_1}$$

From Fig. 4 similar relationships are obtained when more spray headers comes into service.

Spray levels: 1 + 2 + 3:

$$\frac{N_1+\Delta N_2+\Delta N_3}{\alpha_1\alpha_2}=N_1;\Delta N_2=N_1(\alpha_1-1)\Rightarrow\Delta N_3=\alpha_1N_1(\alpha_2-1)$$

$$\begin{aligned}\ln\left(\frac{y_{30}}{y_3}\right) &= \ln\left(\frac{y_{20}}{y'_2}\right)=\Delta N_2+(\Delta N_2+\Delta N_3)\\ &=\ln\left(\frac{y_1}{y_3}\right)-2\ln\left(\frac{y_{in}}{y_1}\right)=(*)\end{aligned}$$

$$\left(\frac{y_{20}}{y_{30}}\right)=\left(\frac{y_1}{y_{20}}\right);y_{30}=\frac{y_{20}^2}{y_1};y_{20}=\frac{y_1^2}{y_{in}}\Rightarrow y_{30}=\frac{(y_1^4/y_{in}^2)}{y_1}=\frac{y_1^3}{y_{in}^2}$$

Thus

$$\begin{aligned}(*) &= \ln\left(\frac{y_1}{y_3}\right)-2\ln\left(\frac{y_{in}}{y_1}\right)=\ln\left(\frac{y_2}{y_3}\right)+\ln\left(\frac{y_1}{y_2}\right)-2N_1\\ &=2\ln\left(\frac{y_1}{y_2}\right)-2N_1+\Delta N_3=2\Delta N_2+\Delta N_3\end{aligned}$$

$$\Delta N_3=\ln\left(\frac{y_2}{y_3}\right)-\ln\left(\frac{y_1}{y_2}\right);\alpha_2=1+\frac{\Delta N_3}{N_1+\Delta N_2}$$

$$\begin{aligned}\frac{G}{(K_Ga)''P}\times\ln\left(\frac{y_{in}}{y_3}\right) &= \frac{G}{(K_Ga)''P}\times[(N_1+\Delta N_2+\Delta N_3)+(N_1+\Delta N_2)+N_1]\\ &= \frac{G}{(K_Ga)_1P}\left[\frac{N_1+\Delta N_2+\Delta N_3}{\alpha_1\alpha_2}+\frac{N_1+\Delta N_2}{\alpha_1}+N_1\right]\end{aligned}$$

$$\begin{aligned}\frac{(K_Ga)''}{(K_Ga)_1} &= \frac{3N_1+2\,\Delta N_2+\Delta N_3}{((N_1+\Delta N_2+\Delta N_3)/\alpha_1\alpha_2)+((N_1+\Delta N_2)/\alpha_1)+N_1}\\ &= \frac{3N_1+2\,\Delta N_2+\Delta N_3}{3N_1} = \frac{N_1(3+2(\alpha_1-1)+\alpha_1(\alpha_2-1))}{3N_1}\end{aligned}$$

$$\left.\begin{array}{l}\dfrac{(K_Ga)''}{(K_Ga)_1} = \dfrac{1+\alpha_1+\alpha_1\alpha_2}{3}\\[2ex] \dfrac{(K_Ga)''_1}{(K_Ga)_1} = \alpha_1\alpha_2\end{array}\right\}\Rightarrow \frac{(K_Ga)''}{(K_Ga)''_1} = \frac{1+\alpha_1+\alpha_1\alpha_2}{3\alpha_1\alpha_2}$$

Spray levels: 1 + 2 + 3 + 4:

$$\frac{N_1+\Delta N_2+\Delta N_3+\Delta N_4}{\alpha_1\alpha_2\alpha_3} = N_1;$$

$$\Delta N_2 = (\alpha_1-1)N_1;\quad \Delta N_3 = \alpha_1(\alpha_2-1)N_1 \Rightarrow \Delta N_4 = \alpha_1\alpha_2(\alpha_3-1)N_1$$

$$\begin{aligned}\ln\left(\frac{y_{40}}{y_4}\right) &= \Delta N_2+(\Delta N_2+\Delta N_3)+(\Delta N_2+\Delta N_3+\Delta N_4)\\ &= 3\,\Delta N_2+2\,\Delta N_3+\Delta N_4 = \ln\left(\frac{y_1}{y_4}\right)-3N_1\end{aligned}$$

$$\left(\frac{y_{30}}{y_{40}}\right) = \left(\frac{y_{20}}{y_{30}}\right) \Rightarrow y_{40} = \frac{y_{30}^2}{y_{20}} = \frac{y_1^6/y_{in}^4}{y_1^2/y_{in}} = \frac{y_1^4}{y_{in}^3}$$

$$\begin{aligned}\ln\left(\frac{y_1}{y_4}\right)-3N_1 &= \ln\left(\frac{y_3}{y_4}\right)+\ln\left(\frac{y_1}{y_3}\right)-3N_1\\ &= 3\ln\left(\frac{y_1}{y_2}\right)-3N_1+2\ln\left(\frac{y_2}{y_3}\right)-2\ln\left(\frac{y_1}{y_2}\right)+\Delta N_4\\ &= 3\,\Delta N_2+2\,\Delta N_3+\Delta N_4\end{aligned}$$

$$\Delta N_4 = \ln\left(\frac{y_3}{y_4}\right)-\ln\left(\frac{y_2}{y_3}\right);\quad \alpha_3 = 1+\frac{\Delta N_4}{N_1+\Delta N_2+\Delta N_3}$$

$$\begin{aligned}&\frac{G}{(K_Ga)'''P}\times\ln\left(\frac{y_{in}}{y_3}\right)\\ &\quad= \frac{G}{(K_Ga)'''P}\times[(N_1+\Delta N_2+\Delta N_3+\Delta N_4)+(N_1+\Delta N_2+\Delta N_3)\\ &\qquad+(N_1+\Delta N_2)+N_1] = \frac{G}{(K_Ga)_1P}\left[\frac{N_1+\Delta N_2+\Delta N_3+\Delta N_4}{\alpha_1\alpha_2\alpha_3}\right.\\ &\qquad\left.+\frac{N_1+\Delta N_2+\Delta N_3}{\alpha_1\alpha_2}+\frac{N_1+\Delta N_2}{\alpha_1}+N_1\right]\end{aligned}$$

$$\begin{aligned}\frac{(K_Ga)'''}{(K_Ga)_1} &= \frac{4N_1+3\,\Delta N_2+2\,\Delta N_3+\Delta N_4}{4N_1}\\ &= \frac{N_1(4+3(\alpha_1-1)+2\alpha_1(\alpha_2-1)+\alpha_1\alpha_2(\alpha_3-1))}{4N_1}\end{aligned}$$

$$\left.\begin{array}{l}\dfrac{(K_Ga)'''}{(K_Ga)_1} = \dfrac{1+\alpha_1+\alpha_1\alpha_2+\alpha_1\alpha_2\alpha_3}{4}\\[2ex] \dfrac{(K_Ga)'''_1}{(K_Ga)_1} = \alpha_1\alpha_2\alpha_3\end{array}\right\}\Rightarrow \frac{(K_Ga)'''}{(K_Ga)'''_1}$$

$$= \frac{1+\alpha_1+\alpha_1\alpha_2+\alpha_1\alpha_2\alpha_3}{4\alpha_1\alpha_2\alpha_3}$$

Appendix C.

In this annex, the procedure applied to obtain Eqs. (17)–(19) is extended to the other parameters regarding with the upper spray headers. Thus, when SL_3 comes into service, the liquid from this spray level is still capable of absorbing SO_2 in the SL_1 zone but less than liquid coming from SL_2. In effect, liquid from SL_3 is more saturated of SO_2 than that from SL_2, and now the relative value to be considered is the following: $(1-\eta_{SL_3})(1-\eta_{SL_2})$. Hence:

$$\begin{aligned}\frac{\Delta N_3}{N_1} &= \left(1-\eta_{SL_3}\right)\left(1-\eta_{SL_2}\right) = \left(1-\frac{y'_2-y_{out}}{y'_2}\right)\left(1-\frac{y''_1-y'_2}{y''_1}\right)\\ &= \left(1-\frac{y_{in}-y_1}{y_{in}}\right)\left(1-\frac{y_{in}-y'_1}{y_{in}}\right) = \frac{y_1}{y_{in}}\times\frac{y'_1}{y_{in}}\\ &= e^{-N_1}\times\frac{y'_1}{y_1}\times\frac{y_1}{y_{in}} = e^{-N_1}e^{-(N_1+\Delta N_2)}\end{aligned}$$

$$\alpha_2 = 1+\frac{\Delta N_3}{N_1+\Delta N_2} = 1+\frac{\Delta N_3/N_1}{1+(\Delta N_2/N_1)} = 1+\frac{e^{-N_1}e^{-(N_1+\Delta N_2)}}{1+e^{-N_1}}$$

$$\frac{(K_Ga)''}{(K_Ga)''_1} = \frac{1+\alpha_1+\alpha_1\alpha_2}{3\alpha_1\alpha_2}$$

For SL_4 the relative value will be $(1-\eta_{SL_4})(1-\eta_{SL_3})(1-\eta_{SL_2})$ and the following expressions are obtained:

$$\begin{aligned}\frac{\Delta N_4}{N_1} &= \left(1-\eta_{SL_4}\right)\left(1-\eta_{SL_3}\right)\left(1-\eta_{SL_2}\right)\\ &= \left(1-\frac{y'_3-y_{out}}{{y_3}'}\right)\left(1-\frac{y''_2-y'_3}{y''_2}\right)\left(1-\frac{y'''_1-y''_2}{y'''_1}\right)\\ &= \left(1-\frac{y_{in}-y_1}{y_{in}}\right)\left(1-\frac{y_{in}-y'_1}{y_{in}}\right)\left(1-\frac{y_{in}-y''_1}{y_{in}}\right)\\ &= \frac{y_1}{y_{in}}\times\frac{y'_1}{y_{in}}\times\frac{y''_1}{y_{in}} = e^{-N_1}e^{-(N_1+\Delta N_2)}\times\frac{y''_1}{{y_1}'}\times\frac{y'_1}{y_1}\times\frac{y_1}{y_{in}}\\ &= e^{-N_1}e^{-(N_1+\Delta N_2)}e^{-(N_1+\Delta N_2+\Delta N_3)}\end{aligned}$$

$$\begin{aligned}\alpha_3 &= 1+\frac{\Delta N_4}{N_1+\Delta N_2+\Delta N_3} = 1+\frac{\Delta N_4/N_1}{1+(\Delta N_2/N_1)+(\Delta N_3/N_1)}\\ &= 1+\frac{e^{-N_1}e^{-(N_1+\Delta N_2)}e^{-(N_1+\Delta N_2+\Delta N_3)}}{1+e^{-N_1}+e^{-N_1}e^{-(N_1+\Delta N_2)}}\end{aligned}$$

$$\frac{(K_Ga)'''}{(K_Ga)'''_1} = \frac{1+\alpha_1+\alpha_1\alpha_2+\alpha_1\alpha_2\alpha_3}{4\alpha_1\alpha_2\alpha_3}$$

For absorbers with various spray levels, the following general expressions could be used:

$$\begin{aligned}\Delta N_k &= \Delta N_{k-1} e^{-\left(N_1+\sum_{i=2}^{k-1}\Delta N_i\right)}\\ &= N_1 e^{-N_1} e^{-\left(\sum_{j=2}^{k-1}\left(N_1+\sum_{i=2}^{j}\Delta N_i\right)\right)} \quad (k \geq 3)\end{aligned}$$

$$\begin{aligned}\alpha_k &= 1+\frac{e^{-N_1}e^{-(N_1+\Delta N_2)}e^{-(N_1+\Delta N_2+\Delta N_3)}\dots e^{-\left(N_1+\sum_{j=2}^{k}\Delta N_i\right)}}{1+e^{-N_1}+e^{-N_1}e^{-(N_1+\Delta N_2)}+\dots+e^{-N_1}e^{-(N_1+\Delta N_2)}e^{-(N_1+\Delta N_2+\Delta N_3)}\dots e^{-\left(N_1+\sum_{j=2}^{k-1}\Delta N_i\right)}}\\ &= 1+\frac{e^{-(kN_1+(k-1)\Delta N_2+\dots+\Delta N_k)}}{1+e^{-N_1}+e^{-N_1}e^{-(N_1+\Delta N_2)}+\dots+e^{-N_1}e^{-(N_1+\Delta N_2)}e^{-(N_1+\Delta N_2+\Delta N_3)}\dots e^{-\left(N_1+\sum_{j=2}^{k-1}\Delta N_i\right)}} \Rightarrow \alpha_k\end{aligned}$$

$$\alpha_k = 1+\frac{e^{-N_1}e^{-\left(\sum_{j=2}^{k}\left(N_1+\sum_{i=2}^{j}\Delta N_i\right)\right)}}{1+e^{-N_1}+\sum_{z=2}^{k-1}e^{-N_1}e^{-\left(\sum_{j=2}^{z}\left(N_1+\sum_{i=2}^{j}\Delta N_i\right)\right)}} \quad (k \geq 3)$$

References

[1] H. Kikkawa, T. Nakamoto, M. Morishita, K. Yamada, New wet FGD process using granular limestone, Ind. Eng. Chem. Res. 41 (2002) 3028–3036.

[2] Y. Zheng, S. Kiil, J.E. Johnsson, Experimental investigation of a pilot-scale jet bubbling reactor for wet flue gas desulphurisation, Chem. Eng. Sci. 58 (2003) 4695–4703.

[3] A. Bandyopadhyay, M.N. Biswas, Critical flow atomizer in SO_2 spray scrubbing, Chem. Eng. J. 139 (2008) 29–41.

[4] F.J. Gutiérrez Ortiz, F. Vidal, P. Ollero, L. Salvador, V. Cortés, A. Giménez, Pilot-plant technical assessment of wet flue gas desulfurization using limestone, Ind. Eng. Chem. Res. 45 (2006) 1466–1477.

[5] H.G. Nygaard, S. Kiil, J.E. Johnsson, J.N. Jensen, J. Hansen, F. Fogh, K. Dam-Johansen, Full-scale measurements of SO_2 gas phase concentrations and slurry compositions in a wet flue gas desulphurisation spray absorber, Fuel 83 (2004) 1151–1164.

[6] A. Gómez, N. Fueyo, A. Tomás, Detailed modelling of a flue-gas desulfurisation plant, Comput. Chem. Eng. 31 (2007) 1419–1431.

[7] C. Brogren, H.T. Karlsson, Modeling the absorption of SO_2 in a spray scrubber using the penetration theory, Chem. Eng. Sci. 52 (1997) 3085–3099.

[8] N.K. Yeh, G.T. Rochelle, Liquid-phase mass transfer in spray contactors, AIChE J. 49 (2003) 2363–2373.

[9] W. Pasiuk-Bronikowska, J. Ziajka, T. Bronikowski, Autoxidation of Sulphur Compounds, E. Horwood & PWN-Polish Scientific Publishers, Warsaw, Poland, 1992.

[10] M. Gerbec, A. Stergarsek, R. Kocjancic, Simulation model of wet flue gas desulphurization plant, Comput. Chem. Eng. 19 (1995) 283–286.

[11] J. Warych, M. Szymanowski, Model of the wet limestone flue gas desulfurization process for cost optimization, Ind. Eng. Chem. Res. 40 (2001) 2597–2605.

[12] J. Warych, M. Szymanowski, Optimum values of process parameters of the “wet limestone flue gas desulfurization system”, Chem. Eng. Technol. 25 (2002) 427–432.

[13] Y. Zhong, X. Gao, W. Huo, Z. Luo, M. Ni, K. Cen, A model for performance optimization of wet flue gas desulfurization systems of power plants, Fuel Process. Technol. 89 (2008) 1025–1032.

[14] J.W. DeVincentis, Modeling of limestone slurry scrubbing in spray towers with forced oxidation, M.S. Thesis, The Univ. of Texas at Austin, USA, 1998.

[15] DOE, Milliken clean coal demonstration project: a DOE assessment, Technical report, U.S. Department of Energy, 2001.

[16] B. Dou, W. Pan, Q. Jin, W. Wang, Y. Li, Prediction of SO_2 removal efficiency for wet flue gas desulfurization, Energy Convers. Manage. 50 (2009) 2547–2553.