# Impact of Variables on Efficiency of Flue Gas Desulphurisation Plant in Longannet Power Station (ScottishPower)

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### Abstract

Flue Gas Desulphurisation (FGD) plant has been recently installed at Longannet Power Station with the aim of removing sulphur dioxide (SO<sub>2</sub>) from the flue gases. The FGD plant produces a reduction of around 94% of the SO2 emissions, contributing to meet the current  $SO_2$  emissions legislation. Therefore, the use of the FGD plant contributes to extend the life of the power station. However, due to the nature of the sea-water scrubbing technology, the FGD plant, it produces an acidic effluent which needs to be controlled to meet the water discharge limits. The aim of this study is to improve the FGD plant efficiency. A thorough study of the FGD process derives to an expression for the pH and dissolved oxygen concentration in the discharge water. It serves to review the influencing factors affecting the efficiency of the FGD plant. In addition, the approximated prediction model derives to a new SO<sub>2</sub> load to flume limit, which is less conservative that the one in use. This would permit an increase of the FGD plant efficiency, minimising costs. Tests are recommended to obtain the unknown parameters in the proposed  $SO_2$  load to flume limit.

Keywords: Coal Fired Power Station / Longannet / FGD / SW scrubbing / Alkalinity / Sulphur dioxide / Effluent

### Nomenclature

А	Seawater alkalinity (mg/l)	iπ <sub>SO2,i</sub>	Unit "i" SO <sub>2</sub> load to flume (kg/h)	
[A]	Seawater alkalinity (M)	m <sub>SO2,max</sub>	Maximum allowable SO <sub>2</sub> load to flume (kg/h)	
В	Constant, equal to 1/23400 (M·m <sup>3</sup> ·h·s <sup>-1</sup> ·kg <sup>-1</sup> )	m <sub>SO2,in</sub>	SO <sub>2</sub> flow arriving to each FGD unit inlet (kg/	
C	Contribution of AS2 to the proposed $SO_2$ load limit (kg/h)	n	Number of blowers in use in the AS2	
C <sup>D</sup> <sub>c</sub>	Total concentration of inorganic carbon in the	$[O_2]$	Oxygen concentration in water (M)	
	outlet of AS2 (M)	$[O_2]_T$	Oxygen solubility in water (M)	
$C^0_c$	Total concentration of inorganic carbon in the	[OH <sup>-</sup> ]	Hydroxide ion concentration (M)	
	inlet of AS2 (M)	pН	Sörensen Exponent	
$C^0_{CO2}$	Initial concentration of carbon dioxide (M)	Q	Water flow $(m^3/s)$	
C <sup>0</sup> <sub>HCO3-</sub>	Initial concentration of bicarbonate ion (M)	$Q_{CW}$	Cooling water flow $(m^3/s)$	
c <sub>1</sub>	Constant, equal to 141.93 kg·mg <sup>-1</sup> ·l·h <sup>-1</sup>	Qin	Heat input (MW)	
c <sub>2</sub>	Constant, equal to 69.12 kg·mg <sup>-1</sup> ·l·h <sup>-1</sup>	S	Sulphur concentration in coal (%)	
[CO <sub>2</sub> ]	Carbon dioxide concentration (M)	[SO <sub>2</sub> ]	Sulphur dioxide concentration increase due to	
$[CO_2]_r$	Carbon dioxide reduction in AS2 (M)	2	absorption (M)	
$[CO_2]_{r,mg/l}$	Carbon dioxide reduction in AS2 (M)	$[SO_3^{2^-}]$	Sulphite ion concentration (M)	
$[CO_3^{2-}]$	Carbonate ion concentration (M)	$[SO_4^{2-}]$	Sulphate ion concentration (M)	
CV	Calorific value of the coal (kJ/kg)	Х	Concentration change due to neutralisation (M)	
D	Constant, equal to $7.2 \cdot 10^6$	у	Fraction of [HCO <sub>3</sub> <sup>-</sup> ] in water discharge over the	
DO	Dissolved Oxygen (%)		total concentration of inorganic carbon	
f <sub>SO2</sub>	Fraction of SO <sub>2</sub> produced by the combustion of	$\Delta_1[\mathrm{H}^+]$	$[H^+]$ increase due to SO <sub>2</sub> absorption (M)	
	coal in relation with the total of products	$\Delta_1[O_2]$	$[O_2]$ increase due to $HSO_3^-$ oxidation (M)	
$[\mathrm{H}^+]$	Hydrogen ion concentration (M)	$\Delta_2[\mathrm{H}^+]$	$[H^+]$ increase due to SO <sub>3</sub> <sup>2-</sup> dissociation (M)	
$[HCO_3^-]$	Bicarbonate ion concentration (M)	Subscripts		
[HSO <sub>3</sub> <sup>-</sup> ]	Bisulphite ion concentration (M)	А	Total absorbed water from seal pits to FGD	
, m <sub>c</sub>	mass flow of coal burned (kg/h)	Ai	Absorbed water from seal pits to FGD unit "i"	
m <sub>so2</sub>	Total SO <sub>2</sub> load to flume (kg/h)	d	Water discharged back to the estuary	
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Di	Water discharged from FGD to flume
EM	Effluent Mixing
i	Number of the operational or FGD unit
in	In the estuary
n	After neutralisation
SP	In the seal pits
SPD	Water in seal pits not absorbed to FGD
1	

## **1. Introduction**

Coal fired power stations, such as Longannet, are one of the major existent energy producers. However, the combustion of coal produces emissions that have the potential to damage the environment and human health, such as sulphur dioxide (SO<sub>2</sub>), Nitrogen Oxides (NO<sub>x</sub>) and Carbon dioxide (CO<sub>2</sub>). Boosted Over Fire Air technology reduces NO<sub>x</sub> emissions by up to 25%. However, the limits of the forthcoming legislations for NO<sub>x</sub> emissions are stricter: 200mg/Nm<sup>3</sup>. Further NO<sub>x</sub> reductions are required, which is under investigation. For the moment, the reduction of CO<sub>2</sub> is associated to the better efficiency of the plant, as less coal is burned.

Flue Gas Desulphurisation (FGD) plant has been recently installed in three of the four generating units with the aim of removing  $SO_2$  from the flue gases. Longannet extracts water from Forth Estuary, which is named cooling water (CW). It is used to condense the exhaust steam from the turbines. As a result, it increases its temperature before being discharged via the seal pits into the flume. A fraction of this is extracted from the seal pits to absorb SO<sub>2</sub> in the FGD plant. As a result, water discharged back to the flume is acidic (pH around 3) and it has oxygen  $(O_2)$ . This water is diluted in the rest of CW and neutralised. Two aeration stations (AS) are installed in the flume in order to increase the neutralisation efficiency and increase the O<sub>2</sub> concentration in water before being discharged back to the estuary with a nominally neutral pH.

The acidity and  $O_2$  concentration in discharge water are restricted by legislation. The limits are: pH higher than 6 and  $O_2$  concentration higher than 75% of its solubility. There are a number of factors that affect the discharge water properties. The amount of  $SO_2$ absorbed by CW is limited by these factors. Since the FGD plant is recently commissioned, the limits imposed for its operation are very conservative. This is demonstrated with the fact that the water pH is much higher than the limited one. As a consequence, the use of the FGD plant is not optimised, as more  $SO_2$  load could be absorbed to the flume leading to reduced emissions to air or providing ScottishPower to utilise higher sulphur content coal which tends to be less expensive. Optimisation of the FGD plant would also allow the option of using fewer Aeration Blowers, thus reducing works power. For this reason, a better understanding of the FGD process is necessary to optimise the use of the FGD plant.

The aim of the project is to review the various influencing factors that impact on the efficiency of the FGD plant, and to build a predictive model to allow ScottishPower to optimise the use of the FGD plant. The primary target is to meet the  $SO_2$  emissions legislation, while contributing to extending the life of a power station that meets the needs for two million homes.

# 2. Predictive model for the discharge water pH and dissolved oxygen

# **2.1. Prediction of the pH and dissolved oxygen in the water discharge to estuary**

The compounds in which this study is focusing are: hydrogen ion (H<sup>+</sup>), oxygen (O<sub>2</sub>), dissolved carbon dioxide (CO<sub>2</sub>), bicarbonate (HCO<sub>3</sub><sup>-</sup>), dissolved sulphur dioxide (SO<sub>2</sub>), bisulphite (HSO<sub>3</sub><sup>-</sup>), sulphite (SO<sub>3</sub><sup>2-</sup>), bisulphate (HSO<sub>4</sub><sup>-</sup>) and sulphate (SO<sub>4</sub><sup>2-</sup>) (Vidal Barrero et al., 2009)<sup>7</sup>. The chemical reactions involved are:

$$SO_2 \cdot H_2 O \rightleftharpoons HSO_3^- + H^+$$
 (R1)

$$HSO_3^- \leftrightarrow SO_3^{2-} + H^+$$
 (R2)

$$2 \operatorname{HSO}_{3}^{-} + \operatorname{O}_{2} \rightleftharpoons 2 \operatorname{HSO}_{4}^{-}$$
(R3)

$$2 \operatorname{SO}_{3}^{-} + \operatorname{O}_{2} \stackrel{\sim}{\rightarrow} 2 \operatorname{SO}_{4}^{-}$$
(R4)

$$CO_2 \cdot H_2 O \rightarrow HCO_3^- + H^+$$
 (R5)

### 2.1.1. Water in the estuary

The evolution of pH is driven by the concentration of  $H^+$ , as shown in equation 1 (Addy et al., 2004)<sup>2</sup>.

$$pH = -\log[H^+] \tag{1}$$

Seawater compounds concentrations are in equilibrium (Emerson and Hedges, 2008)<sup>3</sup>. Seawater (SW) has a pH around 8, which determines the H<sup>+</sup> concentration. All the concentrations in this study are expressed in molarity and are represented between square brackets. It depends on the alkalinity of water and the dissolved

 $CO_2$ . Water alkalinity, [A], is the concentration of  $HCO_3^-$  in the estuary.

The parameter DO measures the saturation level of  $O_2$ in water, in %. It depends on the dissolved  $O_2$ concentration and the solubility of  $O_2$  in water,  $[O_2]_T$ , as displayed in equation 2. Aquatic life needs a high DO to live.

$$DO = \frac{[O_2]}{[O_2]_T} \cdot 100\%$$
<sup>(2)</sup>

The concentration of dissolved  $CO_2$  and carbonate ion  $(CO_3^{2-})$  in SW is neglected for pH around 8 (figure 1). Water after the effluent mixing –pH around 5– has a concentration of dissolved  $CO_2$  and  $HCO_3^{-}$ . On the other hand, the absorption of SO<sub>2</sub> results in  $HSO_3^{-}$ , and water after the effluent mixing has a concentration of  $HSO_3^{-}$  and  $SO_3^{-2-}$  (figure 2).



Figure 1. Carbonate-bicarbonate equilibrium in seawater Source: Seinfeld and Pandis (2006) <sup>5</sup>



### 2.1.2. Water in the seal pits

Sea water (SW) is extracted from the River Forth by 4 CW pumps and it is used as CW in the four units. It is discharged to the four seal pits corresponding to each of the units. The volumetric flow,  $Q_{CW}$ , varies with the tides. However, for the purposes of this study, it is

assumed constant and equal to 22m<sup>3</sup>/s for each of the CW pump.

Water temperature has an important effect in the pH and DO of the discharge water. High temperature results in a lower solubility of gases in water. In consequence,  $CO_2$  would be less soluble, so fewer blowers would be required to increase the pH. Moreover,  $O_2$  would be less soluble, so more blowers would be required to increase the DO.

### Assumption 1: Same water compounds concentration in the 4 seal pits and SW.

The concentration of the compounds in the seal pits is equal to the one in the estuary. Furthermore, water compounds concentration in the 4 seal pits is assumed to be the same. The concentration of the compounds of the water absorbed to the 3 FGD units is identical to the one in the seal pits. Moreover, the concentration of the compounds is equal to the one of water that goes directly from the seal pits to the flume.

### 2.1.3. Water absorbed to each FGD unit

A proportion of CW is absorbed from the seal pits to the operating FGD units. There is one absorber pump for each seal pit, extracting a volumetric flow of  $Q_{Ai}$ . This flow bifurcates into three flows, keeping the same water compounds concentration.

### 2.1.4. Absorption of $SO_2$ in the absorber

SO<sub>2</sub> is absorbed by CW in the absorber of each of the 3 FGD units. This produces variations in the water compounds concentration. In consequence, there is an increase of H<sup>+</sup> concentration, decreasing pH to around 3, and a decrease in the dissolved O<sub>2</sub> concentration. The absorption of SO<sub>2</sub> increases the concentration of SO<sub>2</sub> dissolved in water. This increase of concentration for each unit, [SO<sub>2</sub>]<sub>i</sub>, is a function of the SO<sub>2</sub> load discharged to flume,  $\dot{m}_{SO2,i}$ , and the total volumetric flow extracted from the seal pits to the absorbed, Q<sub>A</sub>.

$$[SO_2]_i = \frac{g_{SO_2 \text{ molecular mass}}}{\underset{\text{litres of water}}{g_{SO_2}}}$$
(3)

 $[SO_2]_i$  needs to be expressed in molarity. Hence, the flow absorbed by the pumps, given in m<sup>3</sup>/s, needs to be expressed in 1/s. In addition, the mass flow of SO<sub>2</sub>, given in kg/h, needs to be expressed in g/s.

(4)

$$[SO_2]_i = \frac{\frac{1}{3.6} \overline{a}_{SO_2}/_{64}}{1000 Q_A} = \frac{1}{230400} \cdot \frac{\dot{m}_{SO_2}}{Q_{A_i}}$$

Equation 5 defines a constant B, and 6 displays the simplified concentration of  $SO_2$ .

$$B = \frac{1}{230400} M \cdot m^3 \cdot \mathbf{h} \cdot s^{-1} \cdot kg^{-1}$$
<sup>(5)</sup>

$$[SO_2]_i = B \cdot \frac{\dot{\mathbf{m}}_{SO_2}}{Q_{A_i}} \tag{6}$$

Thus, the  $SO_2$  concentration in water depends on the  $SO_2$  load to flume and the water absorbed to FGD.

### Assumption 2: Simplification of the FGD reactions

For pH around 3 in the FGD discharge to flume, the concentration of  $SO_2$  and  $SO_3^{2-}$  are neglected compared with the concentration of  $HSO_3^-$ . Moreover, the concentration of  $HCO_3^-$  is neglected compared with the  $CO_2$  concentration. These assumptions imply that the following reactions go in one direction:

1.) According to R1, the increase in dissolved  $SO_2$  due to  $SO_2$  absorption forms  $HSO_3^-$ , which produces an increase in H<sup>+</sup> concentration. This  $HSO_3^-$  concentration increase produces  $SO_3^{2-}$ , as shown in reaction R2.

$$SO_2 \cdot H_2 O \rightarrow SO_3^{2-} + 2H^+$$
 (R6)

The increase in  $[H^+]$  is given by (Abu-Eishah and Babahar, 2011)<sup>1</sup>:

$$\Delta_1[H^+] = 2[SO_2] \tag{7}$$

2.) The whole concentration of  $SO_3^{2-}$  reacts with  $O_2$  content in water to produce  $SO_4^{2-}$ , causing a decrease in the  $O_2$  concentration (Lan et al., 2012)<sup>4</sup>.

$$SO_3^{2-} + \frac{1}{2}O_2 \rightarrow SO_4^{2-}$$
 (R7)

As a result, the decrease in [O<sub>2</sub>] is:

$$\Delta_{1}[O_{2}] = -\frac{1}{2}([SO_{2}^{2-}]_{in} + [SO_{2}])$$
(8)

3.) The whole concentration of  $HCO_3^-$  in reacts with  $H^+$  to produce dissolved  $CO_2$ .

$$HCO_{3}^{-} + H^{+} \rightarrow CO_{2} \cdot H_{2}O$$
 (R8)

As a result, the reduction in  $[H^+]$  is:

$$\Delta_2[H^+] = -[A] \tag{9}$$

Since the pH of water in the estuary is 8,  $H^+$  concentration would be to the order of  $10^{-8}$ . This is

neglected compared with the increase in  $H^+$  concentration, around  $10^{-3}$ , for pH=3. The resultant concentrations of  $H^+$  and dissolved  $O_2$  are:

$$[H^+]_{Di} = 2[SO_2]_i - [A]$$
(10)

$$[O_2]_{Di} = [O_2]_{in} - \frac{1}{2} ([SO_2^{2-}]_{in} + [SO_2]_i)$$
(11)

# 2.1.5. Effluent mixing and aeration stations contribution

Acid water from the 3 FGD units is discharged back to the flume where it is mixed with the CW that is not absorbed to the FGD units,  $Q_{SPD}$ , which is:

$$Q_{SPD} = Q_{CW} - Q_A \tag{12}$$

The value of volumetric flow due to the effluent mixing is  $Q_{CW}$ . The mixing is not instantly homogeneous. For this reason, there is a long distance to the discharge, around 1 mille. Moreover, the Aeration Station 1 (AS1) injects  $O_2$  to promote this mixing, as well as to increase the  $O_2$  concentration in water. As a result, CW neutralises the acidic water. Figure 3 gives a good perspective of the flume where these processes are occurring.



Figure 3. Arial view of the whole station from the east

The  $H^+$  concentration as a result of the effluent mixing is represented as  $[H^+]_{EM}$ . It is obtained from the conservation of  $H^+$ , as follows.

$$Q_{CW}[H^+]_{EM} = \sum_{i=1}^{3} Q_{Ai}[H^+]_{Di} + Q_{SPD}[H^+]_{in}$$
(13)

Using equations 4, 10, 12 and 13, neglecting the  $H^+$  concentration in the inlet, and defining the total  $SO_2$  load to flume is the sum of the  $SO_2$  load to flume from each unit:

$$[H^+]_{EM} = 2B \cdot \frac{\blacksquare_{SO_2}}{Q_{CW}} - \frac{Q_A}{Q_{CW}} [A]$$
(14)

The same principles are applied to the dissolved  $O_2$ .

$$[O_2]_{EM} = [O_2]_{in} - \frac{B}{2} \cdot \frac{\Box_{SO_2}}{Q_{CW}} - \frac{1}{2} \cdot \frac{Q_A}{Q_{CW}} [SO_3^2]_{in}$$
<sup>(15)</sup>

### Assumption 3: Effluent mixing reactions simplification

For pH between 4 and 6, expected along the flume, the  $SO_2$  and  $SO_3^{2-}$  concentrations are neglected. Therefore,  $SO_2$  is not involved in any equilibrium reaction, and the resultant  $SO_3^{2-}$  from the dilution is oxidised into sulphate (R4). Assuming that the oxidation of  $SO_3^{2-}$  goes in one direction, dissolved  $O_2$  concentration after the re-establishment of the chemical equilibrium is:

$$[\mathcal{O}_{\mathbf{2}}]_{AR} = [\mathcal{O}_{\mathbf{2}}]_{in} - \frac{B}{\mathbf{2}} \cdot \frac{\blacksquare_{SO_{\mathbf{2}}}}{Q_{CW}} - \frac{1}{\mathbf{2}} \cdot [SO_{\mathbf{3}}^{\mathbf{2}-}]_{in}$$
(16)

Neutralisation, reaction R5, is produced due to the reduction of  $HCO_3^-$  concentration to form  $CO_2$  dissolved, decreasing the H<sup>+</sup> concentration (Tokumura et al., 2006)<sup>6</sup>.

The initial concentration of  $CO_2$  and  $HCO_3^-$  after  $CO_2$  stripping and before neutralisation are named  $C^0_{CO2}$  and  $C^0_{HCO3-}$ . The initial concentration of hydrogen ion is  $[H^+]_{EM}$  and the change of concentration on each element is named x. Table 1 defines the process.

	CO <sub>2</sub>	HCO <sub>3</sub>	$\mathbf{H}^+$	
Initial concentration	C <sup>0</sup> <sub>CO2</sub>	C <sup>0</sup> <sub>HCO3</sub> -	$[\mathrm{H}^{+}]_{\mathrm{EM}}$	
Change in concentration	х	-X	-X	
Equilibrium concentration	C <sup>0</sup> <sub>CO2</sub> +x	C <sup>0</sup> <sub>HCO3</sub> -x	$[H^+]_{EM}$ -x	

**Table 1. Neutralisation process** 

The CO<sub>2</sub> stripping due to the air injected by the aeration station 2 (AS2) helps in the neutralisation. There is a reduction of CO<sub>2</sub> concentration,  $[CO_2]_r$ . It reduces  $C^0_{CO2}$ , and its correspondent increase in H<sup>+</sup> concentration. The concentrations determining x are:

$$C_{\text{HCO}_{\overline{3}}}^{0} = \left(1 - \frac{Q_A}{Q_{CW}}\right) [A]$$
<sup>(17)</sup>

$$C_{CO_2}^{0} = [CO_2]_{in} + \frac{Q_A}{Q_{CW}}[A] - [CO_2]_r$$
(18)

<u>Assumption 4: Simplification of the expression using</u>  $\underline{CO_2-CO_3^{2-}-HCO_3^{-}}$  equilibrium

The total concentration of inorganic carbon is the sum of the dissolved  $CO_2$  and  $HCO_3^-$  concentrations. In the

estuary this is approximately equal to alkalinity, because the dissolved  $CO_2$  is neglected (Figure 1). The total concentration of inorganic carbon before the  $CO_2$  stripping is represented as  $C_c^{0}$ , and it is equal to the alkalinity. The total concentration of inorganic carbon after the  $CO_2$  stripping is represented as  $C_c^{D}$ . It is verified that the sum of  $C_{CO2}^0$  and  $C_{HCO3}^0$  (equations 17 and 18) is equal to  $C_c^{D}$  (equation 19).

$$C_{c}^{D} = [A] - [CO_{2}]_{r}$$
(19)

The fraction of  $HCO_3^-$  concentration in water discharge over the total concentration of inorganic carbon compounds is defined as y. This fraction, according to figure 1, is a function of the pH. The concentration of  $HCO_3^-$  as a result of the neutralisation is:

$$C_{HCO_{3}}^{0} - x = y([A] - [CO_{2}]_{r})$$
(20)

$$[H^+]_n = x = \left(\mathbf{1} - \frac{Q_A}{Q_{cw}}\right)[A] - y[A] + y[C\mathbf{0}_2]_r \quad (21)$$

$$[H^+]_n = \left(1 - \frac{Q_A}{Q_{CW}} - y\right)[A] + y[C\mathbf{0}_2]_r$$
(22)

Air injected by AS increase the  $O_2$  concentration by  $[O_2]_{AS}$ , which directly depends on the amount of air injected and the water temperature.

### 2.1.6. Water discharge to flume

Discharge [H<sup>+</sup>] is obtained as:

$$[H^+]_d = [H^+]_{EM} - [H^+]_n$$
(23)

$$[H^+]_d = 2B \cdot \frac{\boxtimes_{SO_2}}{Q_{CW}} - (1 - y)[A] - y[CO_2]_r$$
(24)

Finally, pH is obtained from equations 1 and 24:

$$pH_d = -\log\left(2B \cdot \frac{\mathbb{E}_{SO_2}}{Q_{CW}} - (1-y)[A] - y[CO_2]_r\right) \quad (25)$$

On the other hand, the  $O_2$  concentration in the discharge as a result of the water treatment is:

$$[\mathcal{O}_2]_d = [\mathcal{O}_2]_{EM} - [\mathcal{O}_2]_{AS} \tag{26}$$

$$[o_2]_d = [o_2]_{in} - \frac{B}{2} \cdot \frac{\Box_{SO_2}}{Q_{CW}} - \frac{1}{2} \cdot [SO_3^{2-}]_{in} + [o_2]_{AS}$$

Finally, from equations 2 and 27:

$$Do_{d} = \frac{\left( \left[ o_{2} \right]_{in} - \frac{B}{2} \cdot \frac{\Box_{SO_{2}}}{Q_{CW}} - \frac{1}{2} \cdot \left[ So_{3}^{2-} \right]_{in} + \left[ o_{2} \right]_{4S} \right)}{\left[ o_{2} \right]_{7}} \cdot \frac{(28)_{4S}}{100\%}$$

### 2.2. Limits of the water pH prediction model

The prediction model for the discharge water pH <u>cannot</u> be performed. Since the hydrogen concentration in water is equal to  $10^{-pH}$  (equation 1), the magnitude order of the hydrogen concentration in molarity is  $10^{-8}$  in the estuary,  $10^{-3}$  in the FGD discharge to flume, between  $10^{-4}$  and  $10^{-5}$  in the effluent mixing, and  $10^{-6}$  in the discharge to estuary. On the other hand, the magnitude order of the alkalinity is of  $10^{-3}$ , the same as for the SO<sub>2</sub> absorbed on each unit, as shown in equation 29.

$$[SO_2] \sim B \cdot \frac{\blacksquare_{SO_2}}{Q_A} \sim \frac{1}{10^6} \cdot \frac{10^4}{10^1} \sim 10^{-3}$$
(29)

There are a number of assumptions done that permit an approximation of the  $H^+$  concentration calculation in function of the  $SO_2$  absorbed concentration to flume and the alkalinity. These approximations are absolutely not acceptable for the water discharge because the  $H^+$  concentration is to the order to  $10^{-6}$ .

In spite of this limitation, the model confirms the factors affecting the discharge water pH. This is extremely useful in order to understand the process, and to determine the control variables.

### 2.3. Factors affecting the water discharge

- <u>Inlet water</u>. Alkalinity affects pH. Higher alkalinity would result in higher discharge water pH. inlet  $O_2$  and  $SO_3^{2-}$  concentrations affect DO.

- Volumetric flow provided by the CW pumps.

-  $\underline{SO_2}$  load to flume. The higher the  $SO_2$  load is absorbed, the lower the pH and DO in the discharge.

- <u>Number of blowers in operation in AS</u>. The more blowers in operation, the more increase in the pH.

- <u>Water temperature</u>. The lower the water temperature, the more dissolved the gases. As a result AS would not work effectively and more blowers would be required.

No other influencing factors were considered to be as significant as those identified by the model.

# 3. Study of factors affecting the discharge

### 3.1. Seawater alkalinity

SW alkalinity is a very important factor determining the efficiency of the FGD plant. The factors affecting the alkalinity of inlet water are very difficult to predict.

Tides show a periodic behaviour. When the tide is rising, water comes from the sea, resulting in high alkalinity. However, when the tide is decreasing, water comes from the fresh water tributaries around the River Forth, resulting in low alkalinity. Moreover, at mid tide rising a fast and strong reduction of the alkalinity is produced due to recirculation of the discharge water from the flume, as shown in figure 4.



Figure 4. Effect of recirculation on alkalinity

Rain is a very important factor. High precipitation periods produce low alkalinity, causing a reduction in sea water alkalinity and a corresponding reduction in FGD scrubbing efficiency. Other meteorological factors are snow melt, ambient temperature, atmospheric pressure, etc.

Thus, SW alkalinity has three different components:

- Periodic component, depending on tides. Tides determine if more fresh water or sea water is absorbed by the CW pumps.

- Mean value during a period, depending on meteorological factors.

- Intermittent component that provokes alkalinity depletion due to recirculation.

### 3.2. SO<sub>2</sub> load to flume

 $SO_2$  load to flume is the total mass flow of the  $SO_2$  removed by the absorber of each of the 3 FGD units that react with CW. It needs to be lower than the

maximum allowable SO<sub>2</sub> load, which is set depending on the SW alkalinity and the total CW flow.

### 3.2.1. Theoretical calculation of SO<sub>2</sub> load to flume

Coal is burned to produce heat input, which is obtained by multiplying the mass flow of coal burned in kg/h,  $\dot{m}_c$ , and the calorific value of this coal in kJ/kg, CV. The result would be in kJ/h. Since the heat input is expressed in MW, it needs to be multiplied by:

$$\frac{\frac{kJ}{h}}{MW} \cdot \frac{h}{3600s} \cdot \frac{MJ}{1000kJ} = \frac{1}{3.6 \cdot 10^6}$$
(30)

Hence, the heat input is also obtained as:

$$Q_{in} = \frac{1}{3.6 \cdot 10^6} \cdot \dot{m}_c \cdot CV \tag{31}$$

The mass flow of SO<sub>2</sub> released,  $\dot{m}_{SO2,in}$ , is obtained by multiplying the mass flow of coal burned times the fraction of SO<sub>2</sub> produced by the combustion of coal in relation with the total of products,  $f_{SO2}$ .

$$\dot{m}_{SO_{2,in}} = f_{SO_2} \cdot \dot{m}_c \tag{32}$$

 $SO_2$  is produced by the reaction of sulphur and  $O_2$ . The fraction of  $SO_2$  can be obtained knowing the sulphur content in coal, S. The molecular mass of sulphur and  $O_2$  is 32g/mol, and the molecular mass of  $SO_2$  is 64g/mol. The fraction of  $SO_2$  is then the double of the sulphur content in coal.

$$\mathbf{S} + \mathbf{O}_2 \to \mathbf{SO}_2 \tag{R9}$$

$$f_{SO_2} = \frac{64}{32} \cdot S = 2 \cdot S \tag{33}$$

The expression to relate heat input with S, CV and  $\dot{m}_{SO2,in}$  is obtained from equations 31, 32 and 33:

$$Q_{in} = \frac{1}{3.6 \cdot 10^6} \cdot \frac{\dot{m}_{SO_{2,in}} \cdot CV}{2 \cdot S}$$
(34)

The SO<sub>2</sub> mass flow arriving to inlet of each FGD unit is equal to the mass flow of SO<sub>2</sub> released by combustion. Defining the parameter D as  $7.2 \cdot 10^6$ , the SO<sub>2</sub> mass flow is:

$$\dot{m}_{SO_{2,in}} = \frac{D \cdot S}{CV} \cdot Q_{in} \tag{35}$$

The SO<sub>2</sub> load in the inlet of the FGD goes either to the stack or to the flume. The proportion of SO<sub>2</sub> in the untreated gases discharged to flume ( $\eta_f$ ) measures the capacity of the FGD plant to absorb the SO<sub>2</sub>. Therefore, the SO<sub>2</sub> load to the flume coming from coal

burning from each unit is shown in equation 36. The total  $SO_2$  mass flow discharged to the flume is displayed in equation 37.

$$\dot{\mathbf{m}}_{SO_2} = \sum_{i=1}^{3} \left( \eta_f \cdot \dot{\mathbf{m}}_{SO_{2,in}} \right)_i$$
(36)

$$\dot{m}_{SO_2} = \sum_{i=1}^{3} \left( \frac{D \cdot \eta_f \cdot S \cdot Q_{in}}{CV} \right)_i$$
(37)

### 3.2.2. Factors influencing the SO<sub>2</sub> load to flume

Equation 37 defines the different factors influencing the  $SO_2$  load to flume. Hence, these different factors affect the discharge water properties.

- <u>Proportion of SO<sub>2</sub> in the untreated gases discharged</u> to flume. It is given by the percentage of flue gas bypassed to the stack. The higher this percentage is, the lower the SO<sub>2</sub> load to flume.

- <u>Heat input</u>. It determines directly the quantity of coal burned. Heat input is affected by three terms: the sent out power, driven by the energy market; the internal energy used for the aeration station blowers, pumps, etc; and the thermal efficiency.

- <u>Coal</u> used: sulphur content and calorific power. The use of different coals affects the  $SO_2$  load to flume, and thus, the efficiency of the FGD.

### 4. Proposed limit for the SO<sub>2</sub> load to flume

The calculation of the maximum allowed  $SO_2$  load to flume from equation 25 would permit the establishment of a limit that would allow the meeting of the legislation while increasing the efficiency of the FGD plant. Thus, it would permit a more efficient use of the FGD plant.

$$\mathbf{10}^{-pH_{disch}} = \mathbf{2B} \cdot \frac{\overline{\mathbf{0}}_{SO_2}}{Q_{CW}} - (\mathbf{1} - y)[\mathbf{A}] - y[CO_2]_r$$
(38)

The SO<sub>2</sub> load to flume can be determined in function of the desired water discharge pH and the AS contribution. The maximum SO<sub>2</sub> load to flume is established to ensure the compliance with the legislation. This limit is calculated for pH=6, for which it corresponds to y=0.3, pursuant to figure 1. Thus, the maximum SO<sub>2</sub> load to flume, knowing that  $10^{-6}$  is neglected in comparison with the alkalinity, is estimated as:

$$\Xi_{SO_2,max} = \frac{0.7}{2B} \cdot Q_{CW} \cdot [A] + \frac{0.3}{2B} \cdot Q_{CW} \cdot [CO_2]_r$$
(39)

This result is compared with the maximum  $SO_2$  load to flume currently established. To perform this comparison, the total CW flow is fixed as 88 m<sup>3</sup>/s, as it is done with the limit in use. For CW flow below 88 m<sup>3</sup>/s the maximum allowable  $SO_2$  load to the flume is reduced proportionally. Alkalinity is expressed in mg/l, which is represented as A. The molecular mass of alkalinity is 50000mg/mol. The  $CO_2$  reduction concentration is expressed in mg/l, which is represented as  $[CO_2]_{r,mg/l}$ . The molecular mass of  $CO_2$ is 44000mg/mol.

$$A = 50000 \cdot [A] \tag{40}$$

$$[CO_2]_{r,\frac{mg}{7}} = 44000 \cdot [CO_2]_r \tag{41}$$

Two new constants are defined:  $c_1$  and  $c_2$ . It is taken into account that molarity (M) is equal to the ratio moles to litre. The units of the constants can be simplified. However, they remain unchanged because they indicate that the parameters are expressed in the units defined.

$$c_1 = 142 \ kg \cdot mg^{-1} \cdot l \cdot h^{-1} \tag{42}$$

$$c_2 = 69 \ kg \cdot mg^{-1} \cdot l \cdot h^{-1} \tag{43}$$

The contribution of the AS2 to the maximum  $SO_2$  load to flume is defined as C, as shown in equation 44. It is expected to increase with the number of blowers, as more air would be injected in water; and with the water temperature, as  $CO_2$  would be less soluble in water.

$$C = c_2 \cdot \left[CO_2\right]_{r,\frac{mg}{l}} \tag{44}$$

Thus, the proposed SO<sub>2</sub> load to flume limit is:

$$\Box_{SO_2,max} = c_1 \cdot A + C \tag{45}$$

Assuming that the AS are not contributing, C=0, this proposed limit is compared in figure 5 with the limit in use, both for  $88m^3/s$ . The limit proposed from 60 to 80 mg/l of alkalinity is very similar to the limit currently set.



Figure 5. Comparison between the proposed limit without aeration stations contribution and the current limit

Since the contribution of AS is significant, the line would be vertically displaced. This increase in the limit for each value of the alkalinity is equal to C, which depends on the number of blowers in use and the water temperature. Therefore, the limit proposed is much less conservative that the one in use.

The reduction of  $CO_2$  due to AS2 is experimentally obtained. Measurements are proposed for the different parts of the year, because the reduction of  $CO_2$  is expected to depend on the number of blowers in use and the water temperature.

Finally, the  $SO_2$  load to flume also needs to meet the legislation for the dissolved  $O_2$ , as shown in equation 47. This condition is not of concern, as it is expected to be always met.

$$\frac{1}{[o_2]_{\tau}} \cdot \left( [o_2]_{in} - \frac{B}{2} \cdot \frac{B}{g_{cw}} - [so_3^{2-}]_{in} + [o_2]_{AS} \right) \cdot 100\% \stackrel{(46)}{>}_{75}^{75}\%$$

$$B_{so_2} > \frac{2}{B} \cdot Q_{cw} \cdot ([o_2]_{in} - [so_3^{2-}]_{in} + [o_2]_{AS} - 0.75 \cdot [\frac{47}{g_2}]_{\tau})$$

### 5. Further work

There is some further work which is strongly recommended to be performed by ScottishPower, as it may provide further improvements in efficiency.

It is especially recommended to experimentally obtain the AS contribution, previously defined as C. It depends on the reduction of  $CO_2$  dissolved in water through the AS (equation 44). The  $CO_2$  reduction is obtained as the difference between the total concentration of inorganic carbon in the inlet, and the outlet of the AS2. The total concentration of inorganic carbon is the sum of the  $HCO_3^-$  concentration and the dissolved  $CO_2$  concentration in water. The reduction of  $CO_2$  would depend on the number of blowers in use and the water temperature. Therefore, measurements are proposed for the different parts of the year and for moments in which different number of blowers are in use. The objective of this test is to monitor the proposed SO<sub>2</sub> load to flume limit in function of the SW alkalinity, the CW flow, the water temperature of the flume and the number of blowers in use.

Once the proposed  $SO_2$  load to flume limit is totally defined, the study of economic assessments is recommended to optimise the use of the FGD plant. One solution would be the use of fewer blowers in AS2, reducing the  $SO_2$  load to flume limit. The other solution would consist on the production of more  $SO_2$ load to flume. According to equation 40, the increase of  $SO_2$  load to flume can be achieved by 2 means: reduction of bypass to the stack or use of a more inexpensive coal, with higher sulphur content. It is recommended to propose different scenarios and to evaluate all the cost reductions for each one, selecting the most profitable.

## 6. Conclusions

Through the achievement of a prediction model, the manuscript identifies the different factors affecting the pH and dissolved  $O_2$  of the discharge water:  $SO_2$  load to flume; SW alkalinity; CW flow; number of blowers in operation in AS and flume water temperature.

A model for the  $SO_2$  load to flume defines the factors influencing the  $SO_2$  load to flume: the heat input; the percentage of flue gas bypassed to the stack; the sulphur content in coal and the calorific value of the coal used. On the other hand, the factors affecting the alkalinity are tides, recirculation and meteorological factors such as pressure, temperature and rainfall. They are very difficult to predict, which hinders the possibility of building a model for the alkalinity.

An important application of the derived expression for the discharge water pH is the calculation of a new  $SO_2$ load to flume limit. It depends on SW alkalinity, CW flow and aeration station contribution. The aeration station contribution is unknown, but it could be experimentally obtained in function of the number of blowers in use and the flume water temperature. This proposed  $SO_2$  load to flume limit is less conservative that the one in use, which would permit a more efficient use of the FGD plant.

Further work is recommended to ScottishPower in order to obtain the predicted  $SO_2$  load to flume limit, and to optimise the use of the FGD plant.

Although the derived model has not been put into practical application to date, the predicted improvements in plant efficiency are of great interest to Scottish Power and further investigation is planned.

# 7. Ethical statement

<u>Conflict of interest</u>: The authors declare that they have no conflict of interest.

Patients' rights and animal protection statements: This article does not contain any studies with human or animal subjects.

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