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_2) 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_2 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

A	Seawater alkalinity (mg/l)
[A]	Seawater alkalinity (M)
B	Constant, equal to 1/23400 ($M \cdot m^3 \cdot h \cdot s^{-1} \cdot kg^{-1}$)
C	Contribution of AS2 to the proposed SO_2 load limit (kg/h)
C^D_c	Total concentration of inorganic carbon in the outlet of AS2 (M)
C^0_c	Total concentration of inorganic carbon in the inlet of AS2 (M)
C^0_{CO2}	Initial concentration of carbon dioxide (M)
C^0_{HCO3-}	Initial concentration of bicarbonate ion (M)
c_1	Constant, equal to 141.93 $kg \cdot mg^{-1} \cdot l \cdot h^{-1}$
c_2	Constant, equal to 69.12 $kg \cdot mg^{-1} \cdot l \cdot h^{-1}$
$[CO_2]$	Carbon dioxide concentration (M)
$[CO_2]_r$	Carbon dioxide reduction in AS2 (M)
$[CO_2]_{r,mg/l}$	Carbon dioxide reduction in AS2 (M)
$[CO_3^{2-}]$	Carbonate ion concentration (M)
CV	Calorific value of the coal (kJ/kg)
D	Constant, equal to $7.2 \cdot 10^6$
DO	Dissolved Oxygen (%)
f_{SO2}	Fraction of SO_2 produced by the combustion of coal in relation with the total of products
$[H^+]$	Hydrogen ion concentration (M)
$[HCO_3^-]$	Bicarbonate ion concentration (M)
$[HSO_3^-]$	Bisulphite ion concentration (M)
$\dot{m}_c$	mass flow of coal burned (kg/h)
$\dot{m}_{SO2}$	Total SO_2 load to flume (kg/h)

$\dot{m}_{SO2,i}$	Unit "i" SO_2 load to flume (kg/h)
$\dot{m}_{SO2,max}$	Maximum allowable SO_2 load to flume (kg/h)
$\dot{m}_{SO2,in}$	SO_2 flow arriving to each FGD unit inlet (kg/h)
n	Number of blowers in use in the AS2
$[O_2]$	Oxygen concentration in water (M)
$[O_2]_T$	Oxygen solubility in water (M)
$[OH^-]$	Hydroxide ion concentration (M)
pH	Sörensen Exponent
Q	Water flow (m^3/s)
Q_{CW}	Cooling water flow (m^3/s)
Q_{in}	Heat input (MW)
S	Sulphur concentration in coal (%)
$[SO_2]$	Sulphur dioxide concentration increase due to absorption (M)
$[SO_3^{2-}]$	Sulphite ion concentration (M)
$[SO_4^{2-}]$	Sulphate ion concentration (M)
x	Concentration change due to neutralisation (M)
y	Fraction of $[HCO_3^-]$ in water discharge over the total concentration of inorganic carbon
$\Delta_1[H^+]$	$[H^+]$ increase due to SO_2 absorption (M)
$\Delta_1[O_2]$	$[O_2]$ increase due to HSO_3^- oxidation (M)
$\Delta_2[H^+]$	$[H^+]$ increase due to SO_3^{2-} dissociation (M)
Subscripts	
A	Total absorbed water from seal pits to FGD
Ai	Absorbed water from seal pits to FGD unit "i"
d	Water discharged back to the estuary

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. 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_2), Nitrogen Oxides (NO_x) and Carbon dioxide (CO_2). Boosted Over Fire Air technology reduces NO_x emissions by up to 25%. However, the limits of the forthcoming legislations for NO_x emissions are stricter: 200mg/Nm^3. Further NO_x reductions are required, which is under investigation. For the moment, the reduction of CO_2 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_2 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_2 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
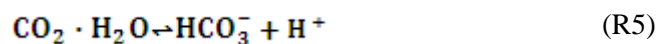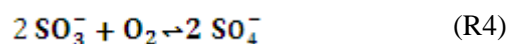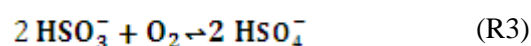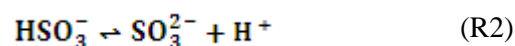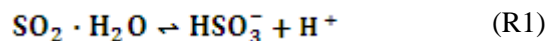
could be absorbed to the flume leading to reduced emissions to air or providing ScottishPower to utilise higher sulphur content coal which tends to be less expensive. Optimisation of the FGD plant would also allow the option of using fewer Aeration Blowers, thus reducing works power. For this reason, 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^+), oxygen (O_2), dissolved carbon dioxide (CO_2), bicarbonate (HCO_3^-), dissolved sulphur dioxide (SO_2), bisulphite (HSO_3^-), sulphite (SO_3^{2-}), bisulphate (HSO_4^-) and sulphate (SO_4^{2-}) (Vidal Barrero et al., 2009)[7]. The chemical reactions involved are:

$$SO_2 \cdot H_2O \rightleftharpoons HSO_3^- + H^+ \tag{R1}$$

$$HSO_3^- \rightleftharpoons SO_3^{2-} + H^+ \tag{R2}$$

$$2\,HSO_3^- + O_2 \rightleftharpoons 2\,HSO_4^- \tag{R3}$$

$$2\,SO_3^- + O_2 \rightleftharpoons 2\,SO_4^- \tag{R4}$$

$$CO_2 \cdot H_2O \rightleftharpoons HCO_3^- + H^+ \tag{R5}$$

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)[2].

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

Seawater compounds concentrations are in equilibrium (Emerson and Hedges, 2008)[3]. Seawater (SW) has a pH around 8, which determines the H^+ 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.

$$DO = \frac{[O_2]}{[O_2]_T} \cdot 100\% \tag{2}$$

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_2 results in HSO_3^-, and water after the effluent mixing has a concentration of HSO_3^- and SO_3^{2-} (figure 2).
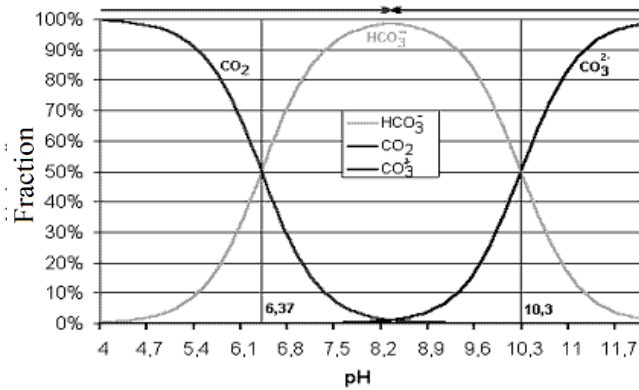

Figure 1. Carbonate-bicarbonate equilibrium in seawater
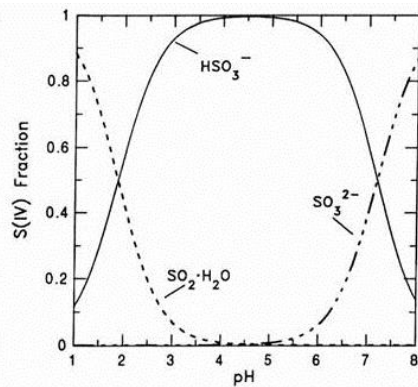**Source: Seinfeld and Pandis (2006)** [5]

Figure 2. Sulphite-bisulphite equilibrium
Source: Seinfeld and Pandis (2006) [5]

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^3/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_2 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^+ concentration, decreasing pH to around 3, and a decrease in the dissolved O_2 concentration. The absorption of SO_2 increases the concentration of SO_2 dissolved in water. This increase of concentration for each unit, $[SO_2]_i$, is a function of the SO_2 load discharged to flume, $\dot{m}_{SO2,i}$, and the total volumetric flow extracted from the seal pits to the absorbed, Q_A.

$$[SO_2]_i = \frac{g/SO_2 \ molecular \ mass}{litres \ of \ water} \tag{3}$$

$[SO_2]_i$ needs to be expressed in molarity. Hence, the flow absorbed by the pumps, given in m^3/s, needs to be expressed in l/s. In addition, the mass flow of SO_2, given in kg/h, needs to be expressed in g/s.

$$[SO_2]_i = \frac{\frac{1}{3.6} \dot{m}_{SO_{2i}} / 64}{1000 \, Q_A} = \frac{1}{230400} \cdot \frac{\dot{m}_{SO_{2i}}}{Q_{Ai}} \tag{4}$$

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

$$B = \frac{1}{230400} M \cdot m^3 \cdot h \cdot s^{-1} \cdot kg^{-1} \tag{5}$$

$$[SO_2]_i = B \cdot \frac{\dot{m}_{SO_{2i}}}{Q_{Ai}} \tag{6}$$

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^+ concentration. This HSO_3^- concentration increase produces SO_3^{2-}, as shown in reaction R2.

$$SO_2 \cdot H_2O \rightarrow SO_3^{2-} + 2H^+ \tag{R6}$$
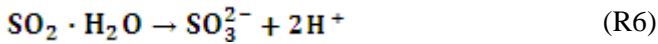
The increase in $[H^+]$ is given by (Abu-Eishah and Babahar, 2011)[1]:

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

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)[4].

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

As a result, the decrease in $[O_2]$ is:

$$\Delta_1[O_2] = -\frac{1}{2}([SO_3^{2-}]_{in} + [SO_2]) \tag{8}$$

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

$$HCO_3^- + H^+ \rightarrow CO_2 \cdot H_2O \tag{R8}$$
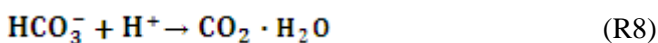
As a result, the reduction in $[H^+]$ is:

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

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:

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

$$[O_2]_{Di} = [O_2]_{in} - \frac{1}{2}([SO_3^{2-}]_{in} + [SO_2]_i) \tag{11}$$

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.

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

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:

$$[H^+]_{EM} = 2B \cdot \frac{\dot{m}_{SO_2}}{Q_{CW}} - \frac{Q_A}{Q_{CW}}[A] \tag{14}$$

The same principles are applied to the dissolved O_2.

$$[O_2]_{EM} = [O_2]_{in} - \frac{B}{2} \cdot \frac{\eta_{SO_2}}{Q_{cw}} - \frac{1}{2} \cdot \frac{Q_A}{Q_{cw}} [SO_3^{2-}]_{in} \qquad (15)$$

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:

$$[O_2]_{AR} = [O_2]_{in} - \frac{B}{2} \cdot \frac{\eta_{SO_2}}{Q_{cw}} - \frac{1}{2} \cdot [SO_3^{2-}]_{in} \qquad (16)$$

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

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_2	HCO_3^-	H^+	
Initial concentration	C^0_{CO2}	C^0_{HCO3-}	$[H^+]_{EM}$	
Change in concentration	x	-x	-x	
Equilibrium concentration	C^0_{CO2}+x	C^0_{HCO3-}-x	$[H^+]_{EM}$ -x	

Table 1. Neutralisation process

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

$$C^0_{HCO_3^-} = \left(1 - \frac{Q_A}{Q_{cw}}\right)[A] \qquad (17)$$

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

Assumption 4: Simplification of the expression using 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^O, 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^0_{CO2} and C^0_{HCO3-} (equations 17 and 18) is equal to C_c^D (equation 19).

$$C_c^D = [A] - [CO_2]_r \qquad (19)$$

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:

$$C^0_{HCO_3^-} - x = y([A] - [CO_2]_r) \qquad (20)$$

$$[H^+]_n = x = \left(1 - \frac{Q_A}{Q_{cw}}\right)[A] - y[A] + y[CO_2]_r \qquad (21)$$

$$[H^+]_n = \left(1 - \frac{Q_A}{Q_{cw}} - y\right)[A] + y[CO_2]_r \qquad (22)$$

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 $[H^+]$ is obtained as:

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

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

Finally, pH is obtained from equations 1 and 24:

$$pH_d = -\log\left(2B \cdot \frac{\eta_{SO_2}}{Q_{cw}} - (1-y)[A] - y[CO_2]_r\right) \qquad (25)$$

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

$$[O_2]_d = [O_2]_{EM} - [O_2]_{AS} \qquad (26)$$

$$[O_2]_d = [O_2]_{in} - \frac{B}{2} \cdot \frac{\eta_{SO_2}}{Q_{cw}} - \frac{1}{2} \cdot [SO_3^{2-}]_{in} + [O_2]_{AS} \qquad (27)$$

Finally, from equations 2 and 27:

$$DO_d = \frac{\left([O_2]_{in} - \frac{B}{2} \cdot \frac{\eta_{SO_2}}{Q_{cw}} - \frac{1}{2} \cdot [SO_3^{2-}]_{in} + [O_2]_{AS}\right)}{[O_2]_r} \cdot 100\% \qquad (28)$$

2.2. Limits of the water pH prediction model

The prediction model for the discharge water pH cannot 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_2 absorbed on each unit, as shown in equation 29.

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

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

- Inlet water. 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.

- SO_2 load to flume. The higher the SO_2 load is absorbed, the lower the pH and DO in the discharge.

- Number of blowers in operation in AS. The more blowers in operation, the more increase in the pH.

- Water temperature. 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.
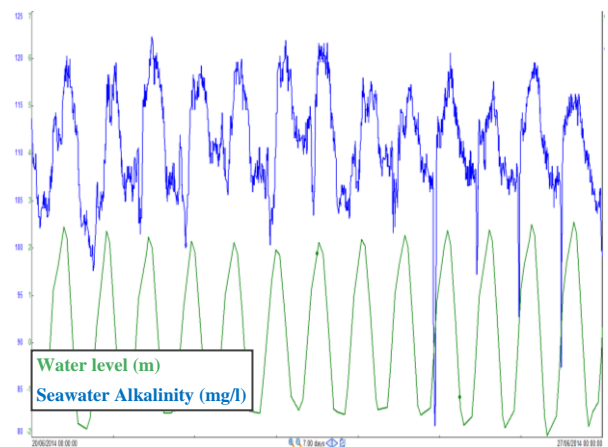

Figure 4. Effect of recirculation on alkalinity

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_2 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_2 load, which is set depending on the SW alkalinity and the total CW flow.

3.2.1. Theoretical calculation of SO_2 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:

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

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_2 released, $\dot{m}_{SO2,in}$, is obtained by multiplying the mass flow of coal burned times the fraction of SO_2 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.

$$S + O_2 \rightarrow SO_2 \tag{R9}$$

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

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

$$Q_{in} = \frac{1}{3.6 \cdot 10^6} \cdot \frac{\dot{m}_{SO_2,in} \cdot CV}{2 \cdot S} \tag{34}$$

The SO_2 mass flow arriving to inlet of each FGD unit is equal to the mass flow of SO_2 released by combustion. Defining the parameter D as $7.2 \cdot 10^6$, the SO_2 mass flow is:

$$\dot{m}_{SO_2,in} = \frac{D \cdot S}{CV} \cdot Q_{in} \tag{35}$$

The SO_2 load in the inlet of the FGD goes either to the stack or to the flume. The proportion of SO_2 in the untreated gases discharged to flume (η_f) measures the capacity of the FGD plant to absorb the SO_2. Therefore, the SO_2 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.

$$\dot{m}_{SO_2} = \sum_{i=1}^{3} \left(\eta_f \cdot \dot{m}_{SO_2,in} \right)_1 \tag{36}$$

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

3.2.2. Factors influencing the SO_2 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.

- Proportion of SO_2 in the untreated gases discharged to flume. It is given by the percentage of flue gas bypassed to the stack. The higher this percentage is, the lower the SO_2 load to flume.

- Heat input. 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.

- Coal 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_2 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.

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

The SO_2 load to flume can be determined in function of the desired water discharge pH and the AS contribution. The maximum SO_2 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_2 load to flume, knowing that 10^{-6} is neglected in comparison with the alkalinity, is estimated as:

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

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^3/s, as it is done with the limit in use. For CW flow below 88 m^3/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.

$$A = 50000 \cdot [A] \qquad (40)$$

$$[CO_2]_{r,\frac{mg}{l}} = 44000 \cdot [CO_2]_r \qquad (41)$$

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.

$$c_1 = 142 \, kg \cdot mg^{-1} \cdot l \cdot h^{-1} \qquad (42)$$

$$c_2 = 69 \, kg \cdot mg^{-1} \cdot l \cdot h^{-1} \qquad (43)$$

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.

$$C = c_2 \cdot [CO_2]_{r,\frac{mg}{l}} \qquad (44)$$

Thus, the proposed SO_2 load to flume limit is:

$$\boxed{\overline{m}_{SO_2,max} = c_1 \cdot A + C \qquad \mathbf{(45)}}$$

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.
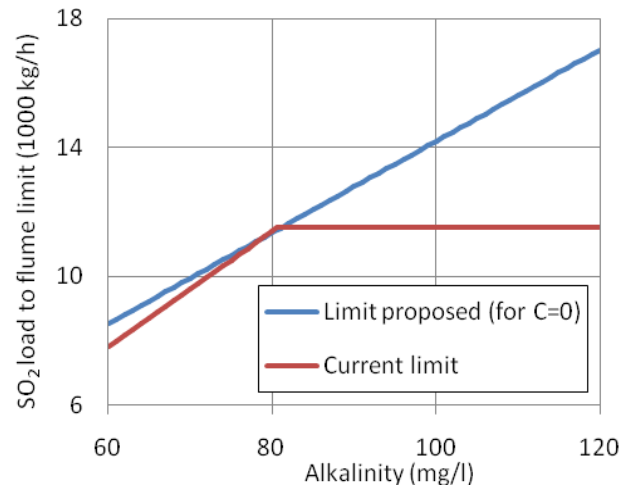

Figure 5. Comparison between the proposed limit without aeration stations contribution and the current limit

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.

$$\frac{1}{[O_2]_r} \cdot \left([O_2]_{in} - \frac{B}{2} \cdot \frac{\overline{m}_{SO_2}}{Q_{CW}} - [SO_3^{2-}]_{in} + [O_2]_{AS} \right) \cdot 100\% > 75\% \qquad (46)$$

$$\overline{m}_{SO_2} > \frac{2}{B} \cdot Q_{CW} \cdot \left([O_2]_{in} - [SO_3^{2-}]_{in} + [O_2]_{AS} - 0.75 \cdot [O_2]_r \right) \qquad (47)$$

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_2 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

Conflict of interest: 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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