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# Use of Seawater Scrubbing for SO<sub>2</sub> Removal from Marine Engine Exhaust Gas

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The mechanism of  $SO_2$  absorption in seawater is treated. Emphasis is on applications of scrubbing of marine engine exhaust gas containing  $SO_2$ . The formulated model is used to predict the influence of various parameters on  $SO_2$  absorption efficiency, e.g., seawater temperature, partial pressure of  $SO_2$ , seawater salinity, and seawater alkalinity. It is found that the absorption capacity of standard seawater is approximately twice that of brackish water with close to zero salinity. The absorption capacity decreases with both decreasing salinity and alkalinity. Different scenarios in which the required water supply rate for a given  $SO_2$  cleaning efficiency is calculated. It is found that a 66% cleaning efficiency, corresponding to meeting the limits of  $SO_x$  emission control areas (SECA) when operating on a fuel containing 4.5% w/w sulfur, requires a minimun water supply rate of 40–63 kg/(kW h) depending on the seawater composition in terms of salinity and alkalinity. Such data are essential in judging the operating cost of seawater scrubbing compared to alternative methods.

#### Introduction

Large marine diesel engines are usually operated on heavy fuel oil, with an average fuel sulfur content of 2.7% w/w.<sup>1</sup> During combustion the fuel sulfur is oxidized mainly to SO<sub>2</sub>. A small fraction of the SO<sub>2</sub> is further oxidized to SO<sub>3</sub>. The conversion fraction depends on many factors, but it is expected to be  $\sim \! 4\%$ , with some variance.<sup>2</sup> The formed SO<sub>3</sub> may react further with water forming sulfuric acid.

Sulfur dioxide emissions impact both human health and the environment. The major health concerns associated with exposure to high concentrations of  $SO_2$  include breathing difficulties and respiratory illness.  $SO_2$  also leads to acid deposition in the environment, i.e., acid rain, causing acidification of lakes and streams and damage to tree foliage and agricultural crops. Furthermore, acid deposition accelerates the decay of buildings and monuments.<sup>3</sup>

According to IMO Annex VI of MARPOL 73/78, Regulations for the Prevention of Air Pollution from Ships,<sup>4</sup> which has been ratified and effectively entered into force from May 2005, the  $SO_x$  emissions are regulated by setting a maximum limiting value on the fuel sulfur content of 4.5% w/w. The  $SO_x$  limit applies to all vessels. In addition to this general regulation, restrictricted areas with tighter regulation have been introduced, a.k.a. SECA ( $SO_x$  emission control areas), which at the moment includes the Baltic Sea. The North Sea and the English Channel are to be included by the end of 2007. In the future the number

of restricted areas is expected to increase. In SECA the following applies according to IMO Annex VI of Marpol 73/78, where at least one of the following conditions shall be fulfilled:

- The sulfur content of the fuel used shall not exceed 1.5% w/w.
- An exhaust gas cleaning system is applied to reduce the total emission of sulfur oxides (including both auxiliary and main propulsion engines) to 6.0 g SO<sub>x</sub>/(kW h) or less (calculated as SO<sub>2</sub>).

The first point requires separate tanks for conventional heavy fuel oil (HFO) and HFO with a sulfur content of 1.5% w/w as well as other technical considerations which should be taken into account.<sup>1</sup> One of the main issues is the availability of low sulfur HFO. If not available, the alternative will be to operate on a distillate fuel at a significantly higher price.<sup>1</sup>

The second point requires the installation of an exhaust gas cleaning/after-treatment system. Conventional methods of removing sulfur oxides from exhaust gas, often referred to as FGD (flue gas desulfurization in relation to power generation), usually involves scrubbing either by dry or wet methods. The wet method is by far the most popular,<sup>3</sup> and usually a slurry of limestone is used as sorbent. Common for most of the methods is the formation of large amounts of byproduct (precipitates) when sulfur oxides react with the sorbent.

A more simple method is the use of seawater for wet scrubbing in order to reduce sulfur oxide emissions.<sup>5,6</sup> Though, only used to a limited extent compared to the conventional FGD methods, this method seems appealing for the following reasons

- No additives needed. The inherent alkalinity of seawater is used as sorbent.
- No byproducts except a slight increase in the natural concentration of sulfate in seawater.

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<sup>(1)</sup> MAN Diesel, *Operation on Low-Sulphur Fuels—Two-Stroke Engines*; MAN Diesel, Copenhagen, 2005 (http://www.mandiesel.dk/article\_005271.html).

<sup>(2)</sup> Engel, P. K.; Thompson, R. E.; Silvestrini, R. Trans. ASME J. Eng. Power 1979, 101, 207–218.

<sup>(3)</sup> Srivastava, R. K.; Jozewich, W.; Singer, C. Environ. Prog. 2001, 20, 219-228.

<sup>(4)</sup> IMO; Annex VI of MARPOL 73/78; Regulations for the prevention of Air Pollution from Ships and NOx technical code, International Maritime Organization, London, 1998.

<sup>(5)</sup> Makkinejad, N.; Kuper, M.; Bohm, H. Process for removing sulphur dioxide from flue gas, United States Patent 5690899, Nov 1997.

<sup>(6)</sup> Oikawa, K.; Yongsiri, C.; Takeda, K.; Harimoto, T. Environ. Prog. 2003, 22, 67–73.

In addition, seawater FGD also appears competitive with conventional FGD methods, when it comes to both capital and operational costs.<sup>6</sup> In a recent survey it was also concluded that, compared to lowering the fuel sulfur content, seawater scrubbing of the exhaust gas was economically superior.<sup>7</sup>

The main purpose of this paper is to investigate the required water amount in order to obtain SO<sub>2</sub> removal efficiencies comparable to that of changing from HFO with high sulfur content to HFO with a fuel sulfur content with less than 1.5% w/w S. Further, the sensitivity of the SO<sub>2</sub> removal efficiency/required water amount on variations in parameters such as seawater composition, scrubber water temperature, etc., is also investigated. Such information, which has not previously been presented, is pivotal in judging the operational costs of seawater scrubbing for SO<sub>2</sub> removal from marine engine exhaust gas.

#### Model

The model for SO<sub>2</sub> absorption in seawater is based on the following reactions being in equilibrium:

$$SO_2(g) = SO_2(aq) \tag{I}$$

$$SO_2(aq) + 2H_2O(1) = HSO_3^-(aq) + H_3O^+(aq)$$
 (II)

$$HSO_3^-(aq) + H_2O(l) = SO_3^{2-}(aq) + H_3O^+(aq)$$
 (III)

$$HCO_3^-(aq) + H_3O^+(aq) = CO_2(aq) + 2H_2O(l)$$
 (IV)

$$CO_2(aq) = CO_2(g)$$
 (V)

Reaction I is the dissolution of gaseous  $SO_2$  in water. In the limit of low solute concentrations the amount of gas dissolved can be expressed by Henry's law,<sup>8</sup> which for  $SO_2$  can be expressed as<sup>9</sup>

$$p_{SO_2} = \frac{[SO_2(aq)]}{k_H}$$
 (1)

where  $p_{SO_2}$  is the partial pressure of  $SO_2$ ,  $[SO_2(aq)]$  is the concentration of sulfur dioxide in the solution (in the following brackets represent total concentration in mol/kg  $H_2O$ , i.e., molality), and  $k_H$  is Henry's constant. The temperature dependency of Henry's constant can be expressed as<sup>11,12</sup>

$$k_{\rm H} = k_{\rm H}^{\rm o} \exp\left(\frac{-\Delta H_{\rm soln}}{R} \left(\frac{1}{T} - \frac{1}{T^{\rm o}}\right)\right) \tag{2}$$

where  $k_{\rm H}{}^{\circ}$  is Henry's constant at the reference state,  $\Delta H_{\rm soln}$  is the enthalpy of solution, T is the temperature in kelvin, and  $T^{\circ}$  is the reference state temperature (298.15 K). Fitting the Henry's constant data reported by Hocking and Lee<sup>9</sup> with eq 2, a value of  $k_{\rm H}{}^{\circ}$  of 1.2 mol/(kg atm) is found and the slope  $-\Delta H_{\rm soln}/R$  is

found to be 2850 K, which is in good agreement with the data compiled by Sander. 11,12

Reaction II is the reaction between dissolved sulfur dioxide and with water, effectively producing bisulfite, 9 where

$$K_{\rm II} = \frac{[{\rm HSO_3}^-][{\rm H_3O}^+]}{[{\rm SO_2(aq)}]}$$
 (3)

is the corresponding first dissociation constant.9

The temperature dependency of  $K_{\rm II}$  can be expressed as<sup>8</sup>

$$K_{\text{II}}(T) = A \exp\left(\frac{-B}{T}\right)$$
 (4)

where the constants A and B may be interpreted as  $\exp(\Delta S^{\circ}/R)$ , with  $\Delta S^{\circ}$  being the standard entropy change associated with reaction II, and correspondingly B can be interpreted as the associated change in standard enthalpy,  $\Delta H^{\circ}$ . The constants are found by fitting eq 4 to the data compiled by Hocking and Lee.

Reaction III is the dissociation of bisulfite to sulfite. At equlibrium

$$K_{\text{III}} = \frac{[\text{SO}_3^-][\text{H}_3\text{O}^+]}{[\text{HSO}_3^-]}$$
 (5)

The temperature dependency of  $K_{\rm III}$  is taken from <sup>13</sup>

$$\ln K_{\text{III}} = -358.57 + 5477.1/T + 65.31 \ln T - 0.1624T \quad (6)$$

Reaction IV is the neutralization of formed bisulfite with the inherent alkainity of seawater. For simplicity, alkalinity will be treated as presence of bicarbonate,  $HCO_3^-$ , only.

$$K_{\text{IV}} = \frac{[\text{CO}_2(\text{aq})]}{[\text{HCO}_3^-][\text{H}_3\text{O}^+]} = K_a^{-1}$$
 (7)

where  $K_{\rm a}$  is the dissociation constant for carbonic acid. The amount of CO<sub>2</sub> dissolved (reaction V) is calculated according to Henry's law (cf. eq 1) with the temperature dependency of Henry's constant from Sander<sup>12</sup> with  $k_{\rm H}{}^{\circ}=0.034$  mol/(kg atm) and  $-\Delta H_{\rm soln}/R=2400$  K.

The influence of temperature and salinity on the value of  $K_a$  has been studied in great detail; see e.g. the work of Mehrbach et al.<sup>14</sup> and Roy et al.<sup>15</sup> and references therein. We will use the empirical correlation presented and validated by Roy et al.<sup>15</sup>

$$\ln K_0 = A + BS^{0.5} + CS + DS^{1.5} + ES^2 \tag{8}$$

where S is salinity and A, B, C, D, and E are functions of temperature

$$A = a_0 + a_1 T + a_2 \ln T (9)$$

The applied coefficients can be found in the work of Roy et al.  $^{15}$ 

According to the empirical extension of the Debye–Hückel equation proposed by Davies, the activity coefficients,  $\gamma$ , can be expressed as a function of the ionic strength, I

$$\log \gamma = -Az^2 \left( \frac{\sqrt{I}}{1 + \sqrt{I}} - 0.2I \right) \tag{10}$$

<sup>(7)</sup> Ritchie, A.; de Jonge, E.; Hugi, C.; Cooper, D. Service Contract on Ship Emissions: Assignment, Abatement and Market-based Instruments. Task 2c - SO<sub>2</sub> Abatement, Final Report for European Commission Directorate General Environment; Entec UK Limited; Aug 2005.

<sup>(8)</sup> Smith, J. M.; Van Ness, H. C.; Abbott, M. M. *Introduction to Chemical Engineering Thermodynamics*, 5th ed.; McGraw-Hill: New York, 1996

<sup>(9)</sup> Hocking, M. B.; Lee, G. W. Water, Air, Soil Pollut. 1977, 8, 255-262.

<sup>(10)</sup> Lide, D. R., Ed.; CRC Handbook of Chemistry and Physics, 78th ed.; CRC Press: Boca Raton, FL, 1997.

<sup>(11)</sup> Sander, R. Compilation of Henry's Law Constants for Inorganic and Organic Species of Potential Importance in Environmental Chemistry, Version 3, 1999 (http://www.henrys-law.org).

<sup>(12)</sup> Sander, R. Henry's Law Constants. In *NIST Chemistry Web-Book*;NIST Standard Reference Database Number 69; Linstrom P. J., Mallard W. G., Eds.; National Institute of Standards and Technology: Gaithersburg, MD, 2005 (http://webbook.nist.gov).

<sup>(13)</sup> Millero, F. J.; Hershey, J. P.; Johnson, G.; Zhang, J.-Z. J. Atmos. Chem. 1989, 8, 377–389.

<sup>(14)</sup> Mehrbach, C.; Culberson, C. H.; Hawley, J. E.; Pytkowicz, R. M. Limnol. Oceanogr. 1973, 18, 897–907.

<sup>(15)</sup> Roy, R. N.; Roy, L. N.; Vogel, K. M.; Porter-Moore, C.; Pearson, T.; Good, C. E.; Millero, F. J.; Campbell, D. C. *Mar. Chem.* **1993**, *44*, 249–267.

Table 1. Major Constituents of Standard Seawater at a Salinity of  $\sim$ 35 ppt<sup>6,17</sup>

C d 112						
	mass fraction	molality				
constituent	(g/kg seawater)	(mol/kg H <sub>2</sub> O)				
Cl-	19.35	0.5658				
Na <sup>+</sup>	10.78	0.4861				
$SO_4^{2-}$	2.71	0.0293				
SO <sub>4</sub> <sup>2-</sup> Mg <sup>2+</sup> Ca <sup>2+</sup>	1.28	0.0548				
Ca <sup>2+</sup>	0.41	0.0107				
$K^{+}$	0.399	0.0106				
HCO <sub>3</sub> <sup>-</sup>	0.108	0.00183				
$Br^{-}$	0.067	0.00087				
Sr <sup>2+</sup>	0.08	0.00009				
$B(OH)_3$	0.0198	0.00033				
$CO_3^{2-}$	0.016	0.00027				
$B(OH)_4^-$	0.0079	0.00010				
F <sup>-</sup>	0.0013	0.00007				

where the ionic strength is calculated as

$$I = \frac{1}{2} \sum ([i]z_i^2) \tag{11}$$

where [i] is is the concentration of ion, i, and  $z_i$  is its corresponding charge. The summation is over all ions in the solution. A in eq 10 is a temperature-dependent coefficient calculated as

$$A = 1.82 \times 10^6 (\epsilon T)^{-3/2} \tag{12}$$

where  $\epsilon$  is the dielectric constant and T is the temperature in kelvin. The Davies equation is applicable to solutions with I < 0.5; however, in this study we will use it for slightly higher I due to its ease of use compared to that of more accurate and elaborate methods such as e.g. the Pitzer interaction model; see e.g. the work of Millero et al.. <sup>13</sup> The ionic strength of seawater is related to its chemical compostion where the main ionic constituents are listed in Table 1.

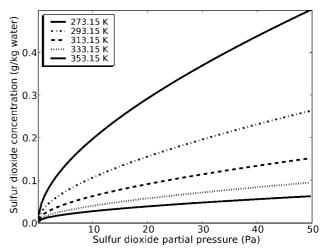
In the calculation of the ionic strength only the most abundant species  $Cl^-$ ,  $Na^+$ ,  $SO_4^{2-}$ ,  $Mg^{2+}$ ,  $Ca^{2+}$ , and  $K^+$  are taken into account. While the salinity shows a clear variation depending on regional location, the relative amounts of the constituents of seawater are more or less invariant  $^{16,17}$ . This is also referred to as the concept of "constant composition of seawater".  $^{17}$  This allows the calculation of ionic strength explicitly as a function of salinity. In order to take the activity coefficients into account the concentration [i] of ion i is replaced with  $\gamma_i[i]$  in the expressions for  $K_{II}$ ,  $K_{III}$ , and  $K_{IV}$ , i.e., eqs 3, 5, and 7.

The equilibrium total concentration of  $SO_2$  in water can be calculated by solving eqs 1, 3, 5, and 7, including Henry's law for  $CO_2$  desorption from water, with the unknowns [HSO<sub>3</sub><sup>-</sup>], [H<sub>3</sub>O<sup>+</sup>], [SO<sub>3</sub><sup>2-</sup>], and [HCO<sub>3</sub><sup>-</sup>]. See e.g. the work of Michalski<sup>18</sup> for details about solving equlibrium equations in relation to gas solubility in aqueous solutions.

## **Results and Discussion**

 $SO_2$  Uptake in Pure Water. The  $SO_2$  uptake has been calculated for pure water, i.e., zero salinity and zero alkalinity. The results of the calculations are shown in Figure 1.

As seen from Figure 1, the total amount of SO<sub>2</sub> absorbed increases with increasing partial pressure. The increase is not



**Figure 1.** Calculated total sulfur dioxide  $(SO_2(aq) + HSO_3^-(aq))$  molality in water as a function of sulfur dioxide partial pressure and temperature.

linear as predicted from Henry's law alone, which is explained by the reaction between dissolved SO<sub>2</sub> and water producing HSO<sub>3</sub><sup>-</sup>. It is also observed that the solubility of SO<sub>2</sub> decreases with increasing temperatures both due to lower solubility of SO<sub>2</sub> but also due to a decreasing dissociation constant with increasing temperature; thus, reaction II is shifted to the left. The results in Figure 1 closely resembles that of Hocking and Lee<sup>9</sup> where the SO<sub>2</sub> solubility in pure water has been calculated for partial pressures of SO<sub>2</sub> up to 10 Pa at various temperatures.

 $SO_2$  Uptake in Seawater. The most important parameter in terms of  $SO_2$  absorption in seawater seems to be the alkalinity<sup>6,19</sup> although other factors may play a vital role as well.<sup>19–21</sup> In the following it will be investigated to which extent the inherent alkalinity in seawater increases its  $SO_2$  absorbing capacity compared to pure water. The total alkalinity can expressed as<sup>17</sup>

$$\begin{split} A_T &= [\text{HCO}_3^{-}] + 2[\text{CO}_3^{2^-}] + [\text{B(OH)}_4^{-}] + [\text{OH}^{-}] + \\ [\text{HPO}_4^{2^-}] + 2[\text{PO}_4^{3^-}] + [\text{SiO(OH)}_3^{-}] + [\text{NH}_3] + [\text{HS}^{-}] + \dots - \\ [\text{H}^+] - [\text{HSO}_4^{-}] - [\text{HF}] - [\text{H}_3 \text{PO}_4] - \dots \ (13) \end{split}$$

and the ellipses represents insignificant contributions either unidentified or in neglectable amounts.

As seen from eq 13 and Table 1, the main contribution to alkalinity is by far HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup>. Ignoring minor contributions the alkalinity for seawater (assuming the composition given in Table 1) can be estimated as  $A_T \approx [HCO_3^{2-}] = 1.83 + 2 \cdot 0.27$ = 2400  $\mu$ mol/kg of H<sub>2</sub>O. The calculated total solubility of SO<sub>2</sub> in seawater, taking the alkalinity into account, i.e., reaction IV, is shown in Figure 2. The starting value of the concentration  $HCO_3^-$  is set at the standard seawater value of  $A_T$ . As seen from the figure, taking alkalinity into account, increases the uptake of SO<sub>2</sub> in seawater compared to that of pure water. The calculated SO<sub>2</sub> uptake in seawater taking both alkalinity and contributions to ionic strength from seawater salinity into account is shown in Figure 3. Table 2 lists the calculated activity coefficients for the involved ionic species as a function of temperature shown for standard seawater (I = 0.72).<sup>17</sup> As seen from Figure 3 and comparing with both Figure 1 for pure water and Figure 2 for seawater with alkalinity both with deviation

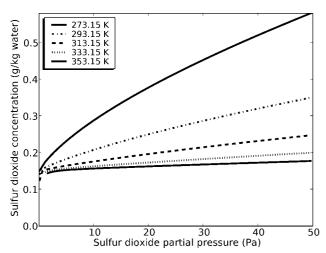
<sup>(16)</sup> Sverdrup, H. U.; Johnson, M. W.; Fleming, R. H. *The Oceans Their Physics, Chemistry, and General Biology*; Prentice-Hall: New York, 1942.

<sup>(17)</sup> Dickson, A. G., Goyet, C., Eds.; Handbook of Methods for the Analysis of the Various Parameters of the Carbon Dioxide System in Sea Water, Version 2, ORNL/CDIAC-74; U.S. Department of Energy: Washington, DC, 1994.

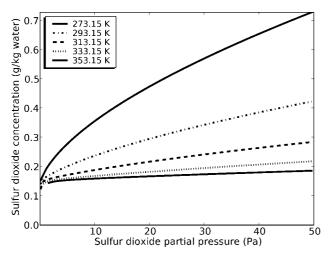
<sup>(18)</sup> Michalski, J. A. Chem. Eng. Technol. 2000, 23, 521-525.

<sup>(19)</sup> Zhao, Y.; Ma, S.-C.; Wang, X.-M.; Zhang, Q. J. Environ. Sci. 2003, 15, 23–128.

<sup>(20)</sup> Vidal, F.; Ollero, P. *Environ. Sci. Technol.* **2001**, *35*, 2792–2796. (21) van den Broeke, W.; Lefers, J. *Chem.-Ing.-Tech.* **1994**, *56*, 792–



**Figure 2.** Calculated total uptake of SO<sub>2</sub> in seawater as a function of partial pressure SO<sub>2</sub> at different temperatures taking the inherent alkalinity of seawater into account.



**Figure 3.** Calculated total uptake of SO<sub>2</sub> in seawater as a function of partial pressure SO<sub>2</sub> at different temperatures taking both the inherent alkalinity of seawater and actual activity coefficients (calculated at standard seawater ionic strength) into account.

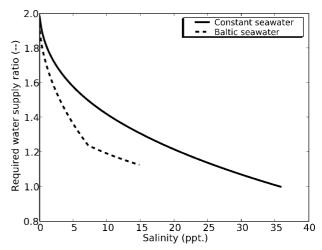
Table 2. Calculated Activity Coefficients of Ionic Species in Seawater Using the Davies Equation  $^a$ 

	0 1			
	acitvity coefficient, $\gamma_i$			
temperature (°C)	$i = \text{HSO}_3^-,$ $\text{HCO}_3^-, \text{H}_3\text{O}^+$	$i = SO_3^{2-}$		
0	0.67	0.20		
20	0.69	0.23		
40	0.72	0.26		
60	0.74	0.30		
80	0.76	0.33		

<sup>&</sup>lt;sup>a</sup> A constant ionic strength of 0.72 is assumed.

from ideality only due to  $SO_2$  absorption, the ionic strength of seawater also increases the  $SO_2$  uptake through more realistic activity coefficients. At the highest temperatures investigated alkalinity seems to be the most important factor in increasing the  $SO_2$  uptake whereas for the lowest temperatures investigated the contribution from ionic strength effects on activity coefficients seems to be the most important factor.

Influence of Seawater Composition on Required Water Supply. In order to investigate the effect of variations in seawater salinity and alkalinity, calculations using the above developed model have been performed. For all calculations the assumptions of a constant seawater temperature of 45 °C and a



**Figure 4.** Calculated required water supply ratio as a function of seawater salinity. The full line is for assumed constant composition of seawater, and the dashed line is for alkalinity/salinity relation for the Kattegat/Baltic Sea estuarine system.

 $SO_2$  partial pressure of 54 Pa, approximately corresponding to a fuel sulfur content of 2.7% w/w and the exhaust gas pressure being close to ambient pressure, have been applied.

Deviations in the relative amounts of the seawater constituents may occur in estuaries/Brackish inland seas where the salinity results from the mixing of fresh water (including dissolved salts from adjoining rivers) with seawater.<sup>22,23</sup> Calculations have been performed both applying the concept of constant seawater composition, i.e., the alkalinity scales linearly with salinity according to the ratio in Table 1 (see e.g. Key et al.<sup>24</sup> and Lee et al.<sup>25</sup> for more elaboration on salinity and alkalinity variations) and applying the relationship between alkalinity and salinity applicable for the Kattegat–Baltic estuarine system.<sup>22</sup>

For the mixing of water in the Gulf of Bothnia with Baltic surface water the following applies

$$A_T = 180S + 177 \tag{14}$$

For the mixing of Baltic Proper water with Kattegat water the following applies

$$A_T = 48S + 1128 \tag{15}$$

The outline of the calculations is the following. For a given salinity the alkalinity is calculated either with the above relations (cf. eqs 14 and 15) or using the constant seawater composition assumption. For the above relations between salinity and alkalinity, the alkalinity is calculated with eq 15 for the higher values of salinity corresponding to mixing between Kattegat water with Baltic Proper water. Lowering the salinity leads to an intersection point between eqs 14 and 15; from this point (and lower values of salinity) eq 14 is used corresponding to mixing between Baltic Proper water with water from the Gulf of Bothnia. For all resulting combinations of salinity and alkalinity the SO<sub>2</sub> uptake capacity is calculated. A required seawater supply ratio is calculated as the ratio between the SO<sub>2</sub> uptake capacity of standard seawater (salinity 35 ppt and alkalinity 2400  $\mu$ mol/

<sup>(22)</sup> Dyrssen, D. Estuaries 1993, 16, 446-452.

<sup>(23)</sup> Wong, G. T. F. Limnol. Oceanogr. 1979, 25, 970-977.

<sup>(24)</sup> Key, R. M.; Kozyr, A.; Sabine, C. L.; Lee, K.; Wanninkhof, R.; Bullister, J.; Feely, R. A.; Millero, F.; Mordy, C.; Peng, T.-H. *Global Biochem. Cycles* **2004**, *18*, GB4031.

<sup>(25)</sup> Lee, K.; Tong, L. T.; Millero, F. J.; Sabine, C. L.; Dickson, A. G.; Goyet, C.; Park, G.-H.; Wannikhof, R.; Feely, R. A.; Key, R. M. *Geophys. Res. Lett.* **2006**, *33*, L19605.

Table 3. Calculated Required Seawater (SW) Supply Rates for 66 and 45% Reduction in SO<sub>2</sub> Emission<sup>a</sup>

location	fuel S (% w/w)	p(SO <sub>2</sub> ) <sub>in</sub> (Pa)	p(SO <sub>2</sub> ) <sub>out</sub> (Pa)	p(SO <sub>2</sub> ) <sub>calc</sub> (Pa)	SO <sub>2</sub> uptake (g/kg)	SO <sub>2</sub> reduc (g/(kW h))	SW amount (kg/(kW h))
A	4.5	90	30	55	0.27	10.8	40
	2.7	54	30	41	0.25	4.1	17
В	4.5	90	30	55	0.27	10.8	49
	2.7	54	30	41	0.20	4.1	22
С	4.5	90	30	55	0.17	10.8	63
	2.7	54	30	41	0.15	4.1	29

<sup>&</sup>lt;sup>a</sup> Calculations are performed for locations A, B, and C with S = 35, 7, and 2 ppt and  $A_T = 2400$ , 1464, and 537  $\mu$ mol/kg, respectively.

kg) divided by the calculated SO<sub>2</sub> uptake capacity for a given combination of salinity and alkalinity.

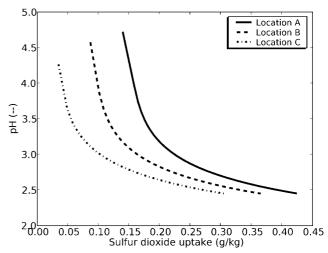
Figure 4 shows the calculated required water supply ratio. The seawater in oceans usually have a salinity  $\pm$  5 ppt of that of standard seawater. According to the figure, going from areas with 35 ppt salinity to areas with 30 ppt the required water amount for a certain SO<sub>2</sub> removal will increase with  $\sim$ 10%.

In the North Sea the salinity is close to that of standard seawater; however, through Kattegat the salinity drops to approximately 10–12 ppt around Sealand. In this area the required water amount is only 20% higher than for standard seawater (dashed line). Going up the Baltic Sea and the Gulf of Bothnia, the salinity drops even further down to a few ppt. As seen from the figure, the required water amount in the Gulf of Bothnia is up to twice the amount of standard seawater.

In the following different scenarios will be evaluated. The first scenario includes a SO2 reduction of 66% by seawater scrubbing, i.e., corresponding to fuel switching from 4.5% to 1.5% w/w sulfur. The minimum required water amount to meet this reduction is calculated at three hypothetical geographic locations. The first location (A) corresponds to standard seawater and could resemble that of the North Sea/English Channel. The second location (B) could resemble that of the Baltic Proper, and the last location (C) roughly corresponds to a location near the bottom (North part) of the Gulf of Bothnia. The second scenario includes a reduction of 45% corresponding to fuel switching from 2.7% (average global fuel sulfur content) to 1.5% w/w sulfur. The results of the calculations are listed in Table 3. The calculations are based on the following assumptions: (i) The required SO<sub>2</sub> reduction (column 7) is based on a specific fuel oil consumption (SFOC) of 180 g/(kW h) (brake power), a reasonable estimate covering both two-stroke and four-stroke diesel engines. (ii) The SO<sub>2</sub> concentration used in the calculations (column 5) is the logarithmic mean of the inlet and outlet concentration.

$$p_{SO_2, calc} = \frac{p_{SO_2, in} - p_{SO_2, out}}{\ln\left(\frac{p_{SO_2, in}}{p_{SO_2, out}}\right)}$$
(16)

The outline of the calculations is the following. Based on the SFOC (g/(kW h)) and the sulfur content of the fuel, the total specific amount of  $SO_2$  (g/(kW h)) can be found both for the actual sulfur content (which is the amount of  $SO_2$  entering the scrubber) and the limiting value of 1.5% w/w (which is the amount of  $SO_2$  leaving the scrubber). The difference between the two is the amount of  $SO_2$  to be removed (in g/(kW h)). The specific amount of  $SO_2$  entering and leaving the scrubber is converted to volumetric concentrations (vol ppm) according to standard data for large two-stroke engines<sup>26</sup> in order to calculate the logarithmic mean  $SO_2$  concentration in the scrubber. From



**Figure 5.** Calculated pH of the scrubber seawater effluent depicted as a function of SO<sub>2</sub> uptake in the water. Calculations have been performed for the seawater compositions of location A, B, and C (see caption of Table 3). A pH value of 8.1 has been assumed for the fresh seawater.

the log mean concentration, the corresponding  $SO_2$  uptake capacity in seawater is found (g/kg). The required water amount is found by dividing the specific amount of  $SO_2$  to be removed (g/(kW h)) with the calculated  $SO_2$  uptake capacity (g/kg).

As seen from Table 3, the required seawater amount ranges from 17 to 63 kg/(kW h) depending on location (salinity, alkalinity) and the fuel sulfur content and hence the required cleaning efficiency. Considering the fact that the usual exhaust gas amount from a two-stroke diesel engine is ~9 kg/(kW h),<sup>26</sup> the calculations clearly show that substantial water amounts are required. An economical survey of the operating cost of seawater scrubbing as an alternative to fuel switching is outside the scope of the present paper. Nevertheless, the numbers in Table 3 are indeed valuable and essential for performing such an analysis.

pH of the Scrubber Seawater Effluent. The pH of the scrubber seawater effluent has been calculated as a function of the seawater SO<sub>2</sub> uptake for different seawater compositions (location A, B, and C), and the results are shown in Figure 5. As seen from the figure, there is a general trend of decreasing pH with increasing SO<sub>2</sub> being absorbed as also inferred from reaction II. A tendency for lower pH at lower alkalinity is also observed as expected due to the corresponding lower neutralizing capacity. The pH value corresponding to the seawater SO<sub>2</sub> uptake listed in Table 3 is in the range 2.5-3, in agreement with that referred by Makkinejad et al.<sup>5</sup> (pH = 2-3), although somewhat lower than the values reported by Oikawa et al.<sup>6</sup> (pH = 3-4.6). This discrepancy may originate from either mass transfer limitations being present in the experiments or the high  $SO_2$  removal efficiency (>90%) reported, resulting in the effective partial pressure of SO<sub>2</sub>, and hence the seawater SO<sub>2</sub> capacity, being lower<sup>6</sup> (see Figure 3). Unfortunately, no data with corresponding scrubber seawater supply rates and SO<sub>2</sub> removal efficiencies have previously been published.

<sup>(26)</sup> Sher, E., Ed.; *Handbook of Air Pollution from Internal Combustion Engines Pollutant Formation and Control*; Academic Press: New York, 1998; pp 477–534.

The construction of the curves in Figure 5 can actually facilitate a method of determining the  $SO_2$  emission reduction efficiency of a seawater scrubber exhaust gas cleaning system alternative to that of direct measurements of the  $SO_2$  gas phase concentration before and after the scrubber. The requirements are detailed knowledge about the seawater alkalinity, scrubber effluent mass flow, exhaust amount, fuel amount, and the assumption of a conversion efficiency of fuel bound S to  $SO_2$ , e.g., 100%.

#### Conclusion

In this paper reduction of SO<sub>2</sub> emissions from large marine diesel engines by seawater scrubbing has been treated. This is

one of the alternatives to switching from a high sulfur content HFO to a lower sulfur content fuel in  $SO_x$  controlled areas (SECA). A model for calculating the seawater  $SO_2$  absorption capacity as a function of a variety of parameters, e.g., partial pressure of  $SO_2$ , seawater temperature, seawater alkalinity, seawater salinity, has been developed. A  $SO_2$  emission reduction of 66%, corresponding to switching from HFO with 4.5–1.5% w/w fuel bound sulfur, has been found to require approximately 40–63 kg of seawater per kW h depending on the salinity and alkalinity of the seawater used in the scrubber. Such data are essential in order to provide a realistic assessment of the operating cost of a seawater scrubber system.

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