Absorption of Sulfur Dioxide in Water with High Salinity

IRINA PINCOVSCHI[1], CRISTINA MODROGAN[2]*

[1]University Politehnica of Bucharest, Faculty of Hydraulic Machinery and Environmental Engineering, Department of Hydraulics, 1-7 Polizu Str., 011061, Bucharest, Romania

[2] University Politehnica of Bucharest, Faculty of Applied Chemistry and Materials Science, Department Analytical Chemistry and Environmental Engineering, 1-7 Polizu Str., 011061, Bucharest, Romania

Understanding the absorption behaviour of sulphur dioxide in aqueous electrolyte solutions is of major interest for the design of flue gas desulphurization processes, as for example wet flue gas desulphurization of coal fired power plants or municipal solid waste incineration plants. In the present paper the influence of the water salinity on SO_2 *absorption is studied. The* SO_2 *absortion was performed in equilibrium condition. The variation of marine solubility from 10 g/L to 40 g/L determines the variation of* SO_2 *concentration in water from 2.6 mol/L to about 3.2 mol/L. In consequence, the variation of water salinity in these limits can detemine a quite big difference of water pollution.*

Keywords: SO_2*, salinity, desulphurization processes*

The importance of studied problem consists in the fact that the majority of planet water is of high salinity varying between 12 g/L (Black Sea) and 35 g/L (Atlantic Ocean). It results that the pollution of such waters with SO_2 is quite different, varying in large limits [1].

Sulfur dioxide is removed from flue gas by absorption processes because of its toxicity. In fossil-fired power plants at the coast, alkaline seawater is often used as a scrubber agent to chemisorb the acid SO_2. In arid regions frequently energy-intensive seawater desalination plants which produce fresh water and brine as a waste product are connected with the power plants. The brine is able to substitute seawater in flue gas desulfurization. However, for the design of such a process, systematic investigations of the influence of ions in the brine on SO_2 absorption are lacking. Hence, a reliable process modeling and prediction of the brine's absorption capacity are not possible. Several working groups have modeled the solubility of SO_2 in sea water on the basis of available models. Abdulsattar [3] has modeled the SO_2 solubility in seawater in a temperature range from 10 to 25 °C. The activity coefficients of the ions were calculated from the Bromley model using an extended Debye–Hückel term [4], and the activity coefficients of the molecularly dissolved components were determined on basis of the coefficients of Rabe and Harris [5] as well as Garrels and Christ [6]. Al-Enezi [7] investigated the solubility of SO_2 in sea water solutions at salinities from 0 to 65 g/kg, temperatures between 10 °C and 40 °C and constant SO_2 partial pressure of 22.4 Pa. The applied model is based on the approach of Abdulsattar [3] and includes an extended Debye–Huckel term to describe the activity coefficients. As a result, a quadratic equation of the SO_2 solubility was fitted as a function of temperature and salinity. However, the equation allows no extrapolations to other SO_2 partial pressures and is therefore limited in their applicability [8-17].

Sulfur dioxide affects the environment in different ways, like direct absorption in water, acid rains and health damages [2, 18-19]. The concentration of SO_2 in residual gases emitted by thermal power plants is about 0.15-0.25%. The SO_2 concentration can to attain bigger values, like in metalurgical ones (1-2 %).

In contrast to the work cited above, in this work the absorption of SO_2 in fundamental binary systems (water + 1 salt) present in seawater was experimentally investigated and modeled first to determine reliable model parameters for the main components of the electrolyte systems seawater.

Theoretical approach

The SO_2 absorption in water is a phisicochemical process developped as follows:

$$SO_2 + H_2O \xleftrightarrow{K_1} H_2SO_3 \xleftrightarrow{K_2} H^+ + $$
$$+ HSO_3^- \xleftrightarrow{K_3} H^+ + SO_3^{2-} \qquad (1)$$

In the equation (1) the proton H^+ represents the strongly hidrated ion H_3O^+.

K_1, K_2 and K_3 representing the equilibrium constants:

$$K_1 = \frac{[H_2SO_3]}{[SO_2]\cdot[H_2O]} \qquad (2)$$

$$K_2 = \frac{[H^+]\cdot[HSO_3^-]}{[H_2SO_3]} \qquad (3)$$

$$K_3 = \frac{[H^+]\cdot[SO_3^{2-}]}{[HSO_3^-]} \qquad (4)$$

where: $[SO_2]$ is the physically absorbed sulfur dioxide concentration;

$[H_2SO_3]$ - the chemically absorbed sulfur dioxide concentration;

$[HSO_3^-]$ - concentration of ions resulting from the first step of H_2SO_3 dissociation;

$[SO_3^{2-}]$ - concentration of ions resulting from the second step of H_2SO_3 dissociation;

$[H^+]$ - hydrogen ion concentration;

$[H_2O]$ - water concentration.

The equilibrium of SO_2 - H_2O system may be appreciated using the equation [12]:

$$p_{SO_{2(e)}} = H\left\{[SO_2]\cdot[H_2SO_3]\right\} \qquad (5)$$

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* email: c_modrogan@yahoo.com

where: $p_{SO2\,(e)}$ represents the equilibrium pressure of sulfur dioxide,

H - Henry constant.

The equation (5) can be transformed in a more explicit form:

$$p_{SO_2(e)} = HS \cdot \frac{1+K_1^{'}}{K_1^{'}} \cdot \frac{\left[H^+\right]^2}{\left[H^+\right]^2 + K_2 \cdot \left[H^+\right] + K_2 \cdot K_3} \qquad (6)$$

where S represents the sum of chemisorbed species:

$$S = \left[H_2SO_3\right] + \left[HSO_3^-\right] + \left[SO_3^{2-}\right] \qquad (7)$$

and

$K_1^{'}$ is the ratio between chemically and physically absorbed species:

$$K_1^{'} = K_1 \cdot \left[H_2O\right] = \frac{\left[H_2SO_3\right]}{\left[SO_2\right]} \qquad (8)$$

Equation (2) highlights the equilibrium concentration of physically absorbed sulfur dioxide:

$$\left[SO_2\right] = \frac{\left[H_2SO_3\right]}{K_1\left[H_2O\right]} = \frac{\left[H_2SO_3\right]}{K_1^{'}} \qquad (9)$$

Combining equations (5) and (9) one obtain:

$$p_{SO_2} = H\left\{\frac{\left[H_2SO_3\right]}{K_1^{'}} + \left[H_2SO_3\right]\right\} = H\left\{\left[H_2SO_3\right] \cdot \frac{1+K_1^{'}}{K_1^{'}}\right\} \qquad (10)$$

The concentration of chemisorbed species $[H_2SO_3]$ can be expressed, combining the relations (3), (4) and (7):

$$\left[H_2SO_3\right] = S \cdot \frac{\left[H^+\right]}{\left[H^+\right]^2 + K_2\left[H^+\right] + K_2 \cdot K_3} \qquad (11)$$

By substituting the equation (11) in (10) we obtain the equation (6). The equilibrium constants $K_2 = 1.7 \times 10^{-2}$ and $K_3 = 6.2 \times 10^{-8}$ from equation (6) have the significance of ionization constants, indicating the H_2SO_3 strength [11]. The low values of ionization constants K_2 and K_3 are indicating the weak character of sulfurous acid (H_2SO_3). Both constants can be used in calculating the proton concentration after the first and the second ionization step, according to equations:

$$\left[H^+\right]_1 = \sqrt{K_2\left[C\right]} \qquad (12)$$

$$\left[H^+\right]_2 = \sqrt{K_3\left[C\right]} \qquad (13)$$

where: $[H^+]_1$ represents the proton concentration after the first step of ionization;

$[H^+]_2$ - the proton concentration after the second step of ionization;

[C] - the total sulfur dioxide concentration in water.

Considering the equation (6) one can see the correlation between SO_2 equilibrium pressure, the solution *p*H and temperature (K_2 and K_3 are functions of temperature). This dependence can be put in evidence experimentally.

Experimental part

The absorbtion of SO_2 in water was experimented in a device presented in figure 1 [16]. It contains a SO_2 measurement vessel (1) having the volume V, an absorption vessel (2) whose volume is v, a mercury manometer (3) and a water manometer (4). The mercury manometer is used for high SO_2 concentrations and the water manometer for low SO_2 concentrations. The order of operations is the following: by slowly opening the tap (8) a vacuum (Δh_1) is made in the vessel (1). Then closing the tap (8) and opening the tap (5) pure SO_2 is introduced, establishing the initial pressure. Closing the tap (5) and opening the tap (9) the communication between the vessel (1) and (2) is established, permitting the SO_2 absorption in the absorbent contained in the vessel (2) till the equilibrium is attained. The SO_2 absorption determines the creation of a vacuum (Δh_2). Knowing Δh_1 and Δh_2 values and the amount of absorbent (g), a point on equilibrium diagram can be represented.

Let's consider the following example. The volume V = 370 cm^3, v = 30 cm^3, Δh_1 = 300 mm Hg, Δh_2 = 53 mm Hg.

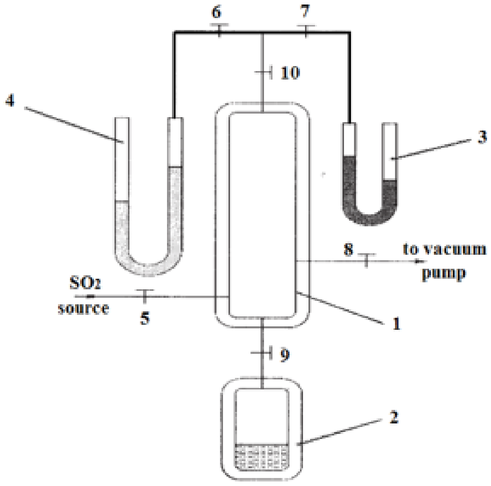

Fig. 1. Experimental device for water-SO_2 equilibrium study 1 - thermostated vessel; 2 -thermostated absorption vessel; 3 - mercury manometer; 4 -water manometer; 5, 6, 7, 8, 9, 10 -taps [16]

In these conditions the SO_2 volume V_T introduced in the vessel (1) is:

$$V_T = V \cdot \frac{\Delta h_1}{P_T} = 370 \cdot \frac{300}{760} = 146\ cm^3$$

where P_T is the total pressure (for example the atmospheric one).

The absorbed SO_2 volume is v_{abs}

$$v_{abs} = \left(V + v\right) \cdot \frac{\Delta h_2}{P_T} = \left(370 + 30\right) \cdot \frac{53}{760} = 27.9\ cm^3$$

The non-absorbed SO_2 volume v_r is

$$v_r = V_T - v_{abs} = 146 - 27.9 = 118.1\ cm^3$$

The equilibrium SO_2 pressure Δh_e is:

$$\Delta h_e = p_e = \Delta h_1 \cdot \frac{V}{V + v} - \Delta h_2 =$$

$$= 300 \cdot \frac{370}{370 + 30} - 53 = 225 \text{ mm Hg}$$

Knowing the amount of absorbent g = 3g H_2O, the SO_2 concentration C_{SO2} can be calculated (in g SO_2/1000 g H_2O) as follows:

$$C_{SO_2} = \frac{27.9\left[cm^3\right]}{22400\left[cm^3 / mol\right]} \cdot 64\left[\frac{g\,SO_2}{mol}\right] \cdot \frac{1000}{3} =$$

$$= 26.5\left[g\,SO_2 / 1000\,g\,H_2O\right]$$

Results and discussions

The experimental method permits to determine the following equluilibrium curves:

1)The dependence of sulfur dioxid concentration in liquide phase, C_{SO2} [mol/L] on sulfur dioxid partial pressure, p_{SO2} [mm Hg] at different water salinity S [g/L] (fig. 2) and

2)The dependence of sulfur dioxid concentration in liquide phase C_{SO2} [mol/L] on water salinity S [g/L]. (fig. 3)

From the figure 2 one can see that the SO_2 cnceentration in liquide phase is decreasing when the salinity S is increasing. This dependence results also from the figure 2. The knowing of these dependences permits to establish tha SO_2 pollution in different conditions.

The results obtained are presented in figure 3 as a equilibrium diagramme between the solubility of water S [g/L] and SO_2 concentration C_{SO2} [mol/L]. The variation of marine solubility from 10 g/L to 40 g/L determines the variation of SO_2 concentration in water from 2.6 mol/L to about 3.2 mol/L. In consequence, the variation of water salinity in these limits can detemine a quite big difference of water pollution.

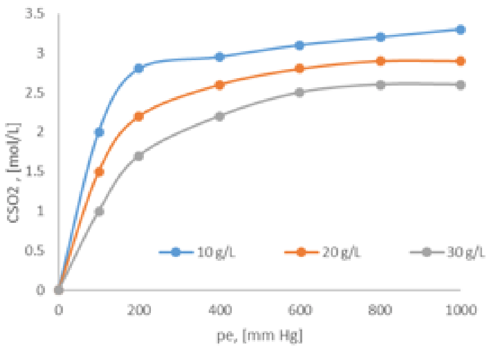

Fig. 2. The dependence of SO_2 concentration in liquide phase, C_{SO2} [mol/L] on SO_2 partial presure p_{SO2} [mm Hg] at different salinity S

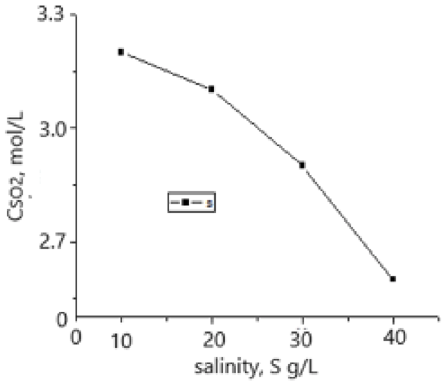

Fig. 3. The dependence of SO_2 concnetration in liquide phase, C_{SO2}, [mol/L] on water salinity, S [g/L]

Conclusions

The study reveals a big influence of salinity of water on SO_2 concentration in water, showing that even at big salinity (40 g/L) the concentration is big enough to create the conditions for natural waters acidification. The SO_2 concentration determined by SO_2 absorption from polluting gases can attain 26.5 g/1000 g water. This concentration is quite low for water acidification because of weak character of H_2SO_3 resulting from SO_2 absorption. Unfortunately in natural waters there are favorable conditions for SO_2 oxidation, conducting finally to H_2SO_4 formation. Only 0.5 H_2SO_4 g/1000g H_2O can determine the value of water *p*H about 3, damaging the fauna and flora. In order to put in evidence the influence of SO_2 partial pressure and temperature on SO_2 concentration in water, equilibrium diagrams have been determined. These diagrams can be also used to design SO_2 absorption devices.

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