Effect of Temperature and Sulfur Dioxide Pressure on Natural Water Pollution

IRINA PINCOVSCHI 1, DANIELA SIMINA STEFAN 2*
1 Politehnica University of Bucharest, Department of Hydraulics, Hydraulic Machinery and Environmental Engineering.
313 Splaiul Independentei, 060042, Bucharest, Romania
2 Politehnica University of Bucharest, Department of Analytic Chemistry and Environmental Protection Engineering, 313 Splaiul Independentei, 060042, Bucharest, Romania

This study presents an investigation concerning the influence of temperature and sulfur dioxide partial pressure on natural water pollution. In order to put in evidence this influence equilibrium diagrams have been determined in a wide range of temperature (10-60°C) covering a sulfur dioxide pressure interval between 50-800 mm Hg. A thermostated vacuum installation has been used permitting the direct pressure measurement at equilibrium. The results show a big influence of temperature on water acidification, especially in the presence of some cations having a catalytic action on sulfur dioxide oxidation.

Keywords: sulfur dioxide absorption, water pollution, water acidification, absorption equilibrium

Sulfur dioxide emissions generated as a result of combustion of fossil fuel, especially in thermal power plants, represent one of the most important atmosphere pollutant. It is estimated that almost 65 million tons of sulfur per year enter the atmosphere, polluting the vegetation and water sources [1, 2]. Big quantities of sulfur dioxide enter the lakes poisoning the flora and the living beings [3].

Sulfur dioxide affects the environmental in different ways like acid rains, corrosion of plants and health damages. The concentration of sulfur dioxide in residual gases emitted by thermal power plants is low (0.15-0.25%). In some industrial plants the sulfur dioxide concentration can attain much bigger values, like in metallurgical ones (1-2%). In such cases the residual gases must be purified using different methods especially alkaline solutions [4-6].

In the present paper the influence of SO2 partial pressure and temperature on water acidification are studied, showing the influence of these parameters on SO2 absorption process in equilibrium conditions.

Theoretical approach

The absorption of sulfur dioxide in water is a physicochemical process, developing according to [7], in the equation (1) the proton H+ represents the strongly hydrated ion H3O+.

\[ SO_2 + H_2O \rightleftharpoons HSO_3^- + H^+ + SO_3^{2-} \]  \hspace{1cm} (1)

\( K_p, K_2 \) and \( K_3 \) representing the equilibrium constants:

\[ K_p = \frac{[HSO_3^-][H^+]}{[SO_2][H_2O]} \]  \hspace{1cm} (2)

\[ K_2 = \frac{[H^+][SO_3^{2-}]}{[HSO_3^-]} \]  \hspace{1cm} (3)

\[ K_3 = \frac{[SO_3^{2-}][H^+]}{[HSO_3^-]} \]  \hspace{1cm} (4)

where:

* email: simina_stefan_ro@yahoo.com

\[ [SO_2] \] 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 [8]:

\[ p_{SO_2} = H ([SO_2] + [H_2SO_3^-]) \]  \hspace{1cm} (5)

where:

\( p_{SO_2} \) represents the equilibrium pressure of sulfur dioxide;
\( H \) - Henry constant.

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

\[ p_{SO_2} = H \left( \frac{1 + K_1}{K_2} \right) \frac{[H^+]}{K_1} + K_2[H_2O] + K_3[H_2O] \]  \hspace{1cm} (6)

where \( S \) represents the sum of chemisorbed species:

\[ S = [H_2SO_3^-] + [HSO_3^-] + [SO_3^{2-}] \]  \hspace{1cm} (7)

and \( K' \) is the ratio between chemically and physically absorbed species:

\[ K' = K_{[H_2O]} = \frac{[H_2SO_3^-]}{[SO_2]} \]  \hspace{1cm} (8)

Equation (2) put in evidence the equilibrium concentration of physically absorbed sulfur dioxide:

\[ [SO_2] = K_p [H_2O] = \frac{[H_2SO_3]}{K_p} \]  \hspace{1cm} (9)

Combining equations (5) and (9) one obtain:
The concentration of chemisorbed species $[H_2SO_3]$ can be expressed, combining the relations (3), (4) and (7):

$$[H_2SO_3] = S \frac{[H^+]^2}{[H^+] + K_1[H^+] + K_2K_3}$$  \hspace{1cm} (11)

By substituting the equations (11) in (10) one 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 [7].

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:

$$[H^+]_1 = \frac{C}{K_2}$$ \hspace{1cm} (12)

$$[H^+]_2 = \frac{C}{K_3}$$ \hspace{1cm} (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 pH and temperature ($K_2$ and $K_3$ are functions of temperature).

This dependence can be put in evidence experimentally.

**Experimental part**

The adopted equipment for water-$SO_2$ equilibrium study (fig.1) 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 ($\Delta h_1$) 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 ($\Delta h_2$). Knowing $\Delta h_1$ and $\Delta h_2$ 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$^3$, $\Delta h_1 = 300$ mm Hg, $\Delta h_2 = 53$ mm Hg. In these conditions the $SO_2$ volume $v_r$ introduced in the vessel (1) is:

$$V_r = V \frac{\Delta h_1}{P_r} = \frac{370 \times 300}{760} = 146 \text{ cm}^3$$

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

The absorbed $SO_2$ volume is $v_{abs}$

$$v_{abs} = (V + v) \frac{\Delta h_1}{P_r} = \frac{(370 + 30) \times 53}{760} = 27.9 \text{ cm}^3$$

The non-absorbed $SO_2$ volume $v_r$ is

$$v_r = V + v - v_{abs} = 146 - 27.9 = 118.1 \text{ cm}^3$$

The equilibrium $SO_2$ pressure $\Delta h_1$ is:

$$\Delta h_1 = P_r - \Delta h_2 = \frac{370}{370 + 30} \times 300 = 225 \text{ mm Hg}$$

Knowing the amount of absorbent $g = 3 \text{ g H}_2\text{O}$, the $SO_2$ concentration $C_{SO_2}$ can be calculated (in g $SO_2$/1000 g H$_2$O) as follows:

$$C_{SO_2} = \frac{27.9 \text{ cm}^3}{22400 \text{ cm}^3/\text{mol}} \times \frac{[gSO_2]}{\text{mol}} \times \frac{1000}{3} = 26.5$$

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

Fig. 2. Correlation between sulfur dioxide concentration in liquid phase $C_{SO_2}$ and partial $SO_2$ pressure $p_{SO_2}$ at equilibrium

The obtained point on the equilibrium diagram in coordinates $C_{SO_2}$ [g/L]-$p_{SO_2}$ [mm Hg] is (26.5; 225).

In the same manner can be calculated the other points on the equilibrium diagram (fig. 2).

**Results and discussions**

The equilibrium diagrams of water-$SO_2$ system, obtained using the installation described in figure 1, are presented in figure 2. One can notice the big influence of temperature and $SO_2$ pressure on $SO_2$ concentration in water. This influence can be put better in evidence examining the diagrams presented in figure 3. At low temperatures the water pollution can be important even at low pressure. For instance, at 10°C and 20 mm Hg, the $SO_2$ concentration in
water can attain 5g/1000g H₂O. The SO₂ concentration in air corresponding to 20 mm Hg is about 2.6%.

The concentration of SO₂ emitted by thermal power plants is low (0.2-0.25%), rarely surpassing 0.4%. The partial SO₂ pressure corresponding to this concentration is about 1.5 mm Hg and 3 mm Hg for 0.2% and 0.4% SO₂ respectively. Experimentally has been shown that using gases containing 0.2% SO₂ the equilibrium concentration of SO₂ in water can attain 0.32g SO₂/1000g H₂O at 10°C. In such conditions the water acidification is insignificant. For instance if the initial water pH is 7, after SO2 absorption the pH decreases to 6.7. Unfortunately in atmospheric conditions the water pH in similar conditions can attain values between 2.5—3.0. In Finland, for instance, the major part of lakes has become “dead” due to the atmospheric conditions, the polluting gases emitted by North England power plants being directed to Scandinavian lands.

The explanation of this phenomenon is the following. The presence in water, even in traces, of some metals like Zn²⁺ and Fe²⁺ can determine the catalytic reactions, [9, 10]:

\[ \text{Zn} + O_2 + H_2O \rightarrow \text{Zn(OH)}_2 \]  
\[ \text{Fe}^{2+} + H_2O \rightarrow \text{Fe}^{3+} + HO^- + H^+ \]  
\[ \text{Fe}^{3+} + HO_2 \rightarrow \{\text{Fe(OOH)}\}^{1+} + H^+ \]  
\[ \{\text{Fe(OOH)}\}^{1+} \rightarrow \text{Fe}^{2+} + HO_2^- \]  

The reaction (15) determines the formation of HO* radicals (Fenton effect), [11, 12] having a strong oxidation character. The same oxidative character have the HO₂ radicals, formed according to reaction (17).

The oxidative character of HO* and HO₂ radicals determines the SO₂ oxidation to SO₃, [13]:

\[ \text{SO}_2 + 2\text{HO}^- \rightarrow \text{SO}_3 + \text{H}_2\text{O} \]  

producing the water acidification [14,15].

Theoretically the oxidation degree of SO₂ to SO₃ can attain 99.9% at equilibrium. Considering the example presented above, the absorbed SO₂ (0.32g SO₂/1000g H₂O) correspond to about 0.49g H₂SO₄/1000g H₂O₂. So, the pH value can decrease from 6.7 to 3. That’s why the water acidification can occur even at very low SO₂ concentrations, specific to power plants polluting gases.

Conclusions

The study reveals a big influence of sulfur partial pressure and temperature on SO₂ concentration in water, showing that even at low SO₂ partial pressure and increased temperatures the SO₂ concentration is big enough to create the conditions for natural waters acidification.

The SO₂ concentration determined by SO₂ absorption from polluting gases can attain 0.3-0.5 g/1000g H₂O. This concentration is quite low for water acidification because of weak character of H₂SO₃ resulting from SO₂ absorption. Unfortunately in natural waters there are favorable conditions for SO₂ oxidation, conducting finally to H₂SO₄ formation. Only 0.5 H₂SO₄ g/1000g H₂O can determine the value of water pH about 3, damaging the fauna and flora.

In order to put in evidence the influence of SO₂ partial pressure and temperature on SO₂ concentration in water, equilibrium diagrams have been determined. These diagrams can be also used to design SO₂ absorption devices.

References