Supporting Information

Mass transfer characteristics and optimization of hydrophilic ceramic membrane contactor for SO_2 absorption

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1 Mass transfer model

1.1 Shell

The mass transfer of SO_2 in the gas phase without reaction follows Fick's law, so its continuum equation is:

$$D_{SO_2\text{-Gas}}\left[\frac{\partial^2 c_{SO_2\text{-Shell}}}{\partial r^2}+\frac{1}{r}\frac{\partial c_{SO_2\text{-Shell}}}{\partial r}+\frac{\partial^2 c_{SO_2\text{-Shell}}}{\partial z^2}\right]-U_{\text{Shell}}\frac{\partial c_{SO_2\text{-Shell}}}{\partial z}=0 \quad (1)$$

where $D_{SO_2\text{-Gas}}$ is the diffusion coefficient of SO_2 in the SO_2/N_2 mixture, 1.23×10^{-5} $m^2\cdot s^{-1}$ at 293.15 K and 1 atm, and U_{Shell} is the gas axial flow rate, $m\cdot s^{-1}$.

Since the gas flow was assumed to be laminar in a concentric tube, the axial gas flow velocity distribution can be calculated as follows:

$$U_{\text{Shell}}(r)=-\frac{8U_{\text{ave-Shell}}}{(r_{\text{shell}}-r_{\text{out}})^2}(r-r_{\text{out}})(r-r_{\text{shell}}) \quad (2)$$

where r_{out} is the outer radius of the ceramic membrane tube, m; r_{shell} is the inner radius of the membrane module, m; and $U_{\text{ave-shell}}$ is the average flow velocity of the gas at the shell side, $m\cdot s^{-1}$, and can be calculated as follows:

$$U_{\text{ave-shell}}=\frac{Q_G}{\pi(r_{\text{shell}}^2-r_{\text{out}}^2)} \quad (3)$$

where Q_G is the gas volume flow, $m^3\cdot s^{-1}$.

The boundary conditions of the mass transfer equation are presented as follows:

$$r=r_{\text{shell}},\quad \frac{\partial c_{SO_2\text{-Shell}}}{\partial r}=0 \quad (4a)$$

$$r=r_{\text{out}},\quad c_{SO_2\text{-Shell}}=c_{SO_2\text{-Membrane}}/m \quad (4b)$$

$$z=L,\quad c_{SO_2\text{-Shell}}=c_0 \quad (4c)$$

where c_0 is the SO_2 concentration at the inlet, $mol\cdot m^{-3}$; $c_{SO_2\text{-Support}}$ is the SO_2

concentration at the pore entrance from the macroporous support, mol·m^{-3}; and L is the length of the membrane tube, m.

1.2 Inside the membrane pores (wetting)

In general, a ceramic membrane is asymmetric and composed of a support layer and a membrane layer. The two layers have different pore sizes and thicknesses, resulting in different diffusion coefficients. The mass transfer of SO_2 in the nonwetted membrane pores can be considered to be diffusion without convection. The hydrophilic membrane pores are filled with a NaOH solution as compared to the hydrophobic membrane. Therefore, SO_2 will react with NaOH in the membrane pores. The continuity equations of SO_2 diffusion through the support layer and the membrane layer are presented as follows:

$$D_{\mathrm{SO_2\text{-}Membrane}}\left[\frac{\partial^2 c_{\mathrm{SO_2\text{-}Membrane}}}{\partial r^2}+\frac{1}{r}\frac{\partial c_{\mathrm{SO_2\text{-}Membrane}}}{\partial r}+\frac{\partial^2 c_{\mathrm{SO_2\text{-}Membrane}}}{\partial z^2}\right]+R_{\mathrm{SO_2}}=0 \qquad (5)$$

where $D_{\mathrm{SO_2\text{-}Membrane}}$ is the diffusion coefficient of SO_2 in the membrane layer, m^2·s^{-1}.

For the wetted membrane, the mass transfer coefficient of the support and membrane layer is determined by the pore structure of the membrane, including the porosity and the tortuosity of the membrane, and the diffusion in membrane pores.

$$D_{\mathrm{SO_2\text{-}Membrane}}=\frac{D_{\mathrm{SO_2\text{-}Water}}\,\varepsilon}{\tau} \qquad (6)$$

where $D_{\mathrm{SO_2\text{-}Water}}$ is the diffusion coefficient of SO_2 in water, 2×10^{-9} m^2·s^{-1} at 20°C, ε is the porosity of the ceramic membrane tube and τ is the tortuosity of the membrane.

The hydroxide ion (OH^-), as another reactant, also diffuses in the membrane layer and reacts with SO_2 to reach a steady state process. Therefore, its mass transfer equation can be presented as follows:

$$D_{\mathrm{OH^-\text{-}Membrane}}\left[\frac{\partial^2 c_{\mathrm{OH^-\text{-}Membrane}}}{\partial r^2}+\frac{1}{r}\frac{\partial c_{\mathrm{OH^-\text{-}Membrane}}}{\partial r}+\frac{\partial^2 c_{\mathrm{OH^-\text{-}Membrane}}}{\partial z^2}\right]+R_{\mathrm{OH^-}}=0 \tag{7}$$

where $D_{\mathrm{OH^-\text{-}Membrane}}$ is the diffusion coefficient of OH^- in the membrane layer, $m^2 \cdot s^{-1}$ and it can be calculated as follows:

$$D_{\mathrm{OH^-\text{-}Membrane}}=\frac{D_{\mathrm{OH^-\text{-}Water}}\varepsilon}{\tau} \tag{8}$$

where $D_{\mathrm{OH^-\text{-}Water}}$ is the diffusion coefficient of OH^- in water, 5.25×10^{-9} $m^2 \cdot s^{-1}$ at 20°C

The boundary conditions of the mass transfer equations are presented as follows:

$$z=0\ or\ L,\quad \frac{\partial c_{\mathrm{SO_2\text{-}Membrane}}}{\partial z}=0 \tag{9a}$$

$$r=r_{\mathrm{in}},\quad c_{\mathrm{SO_2\text{-}Membrane}}=c_{\mathrm{SO_2\text{-}Tube}},\quad c_{\mathrm{OH^-\text{-}Membrane}}=c_{\mathrm{OH^-\text{-}Tube}} \tag{9b}$$

$$r=r_{out},\quad c_{\mathrm{SO_2\text{-}Membrane}}=mc_{\mathrm{SO_2\text{-}Shell}},\quad \frac{\partial c_{\mathrm{OH^-\text{-}Membrane}}}{\partial r}=0 \tag{9c}$$

where m is the phase equilibrium constant of SO_2 in NaOH solution, and r_{in} is the inner radius of the ceramic membrane tube, m.

When a chemical reaction occurs, the absorption process will be greatly enhanced. The phase equilibrium constant which chemical absorption occurs can be calculated by the chemical absorption enhancement factor E.

$$m=\frac{m_{\mathrm{SO_2\text{-}H_2O}}}{E} \tag{10}$$

$$E=\frac{J_{\mathrm{chem}}}{J_{\mathrm{phy}}}=Ha^*=\frac{\sqrt{k_E D_{\mathrm{SO_2\text{-}Membranel}} c^{\mathrm{A}}_{\mathrm{SO_2\text{-}Interface}} c^{\mathrm{1\text{-}A}}_{\mathrm{OH^-\text{-}Interface}}}}{k_{\mathrm{L}}} \tag{11}$$

where k_{L} is liquid phase mass transfer coefficient, $D_{\mathrm{SO_2\text{-}Membrane}}$ is the diffusion coefficient of SO_2 in membrane, $c_{\mathrm{SO_2\text{-}Interface}}$ and $c_{\mathrm{OH^-\text{-}Interface}}$ are the concentrations of

SO_2 and OH^- at the gas-liquid interface, respectively. It is assumed that the reaction of SO_2 with OH^- is as follows,

$$\mathrm{SO_2 + OH^- \xrightarrow{k_E} HSO_3^-} \qquad k_\mathrm{E} = 1.0\times10^6\,\mathrm{m^3/mol}$$

where k_E is a reaction constant. Therefore, the consumption of SO_2 and OH- is equal. The concentration of OH^- at the interface can be calculated as follows:

$$N_{\mathrm{OH^-}} = k_\mathrm{L}(c_{\mathrm{OH^-\text{-}Liquid}} - c_{\mathrm{OH^-\text{-}Interface}}) \tag{12}$$

Since the membrane is filled with liquid, there is no Knudsen diffusion in the pores of the membrane. The thickness of the membrane layer is much larger than the thickness of the liquid phase boundary layer, so it can be considered that k_L can be expressed as[4]:

$$k_\mathrm{L} = \frac{D_{\mathrm{OH^-\text{-}Liquid}}\varphi}{\tau l_{Membrane}} \tag{13}$$

where $D_{\mathrm{OH\text{-}\text{-}Liquid}}$ is the diffusion coefficient of OH^- in liquid, $5.25\times10^{-9}\mathrm{m^2/s}$ at 293.15 K and 1 atm[31], φ is the porosity, τ is the tortuous factor and l_Membrane is the thickness of the membrane.

Similarly, the concentration of SO_2 at the interface can be calculated as the following equation:

$$N_{\mathrm{SO_2}} = -D_{\mathrm{SO_2}}\frac{c_{\mathrm{SO_2\text{-}Gas}} - c_{\mathrm{SO_2\text{-}Interface}}}{\delta_\mathrm{Gas}} = k_\mathrm{g}(c_{\mathrm{SO_2\text{-}Gas}} - c_{\mathrm{SO_2\text{-}Interface}}) \tag{14}$$

where k_g is gas phase mass transfer coefficient. In membrane contactors, the Sherwood number is usually related to the Reynolds number(Re) and the Schmidt number(Sc). When the gas and the liquid flow in a laminar flow($Re<1000$) in a circular straight tube, it can be written as follows[32-34]:

$$Sh = \frac{k_\mathrm{g}L}{D_{\mathrm{SO_2\text{-}Gas}}} = BRe^\mathrm{C}Sc^{0.33} \tag{15}$$

Where L is the length of membrane tube $D_{SO_2\text{-Gas}}$ is the diffusion coefficient of SO_2 in N_2, 1.23×10^{-5} m²/s at 293.15 K and 1 atm[35], B and C are constant. These parameters depend on the configuration of the membrane contactor and the velocity of the gas.

1.3 Tube

The dilution of SO_2 and OH^- in water follows Fick's law. Therefore, the continuity equation of SO_2 and OH^- transport at the tube side under steady-state conditions can be expressed as:

$$R_{SO_2} + D_{SO_2\text{-Water}}\left[\frac{\partial^2 c_{SO_2\text{-Tube}}}{\partial r^2} + \frac{1}{r}\frac{\partial c_{SO_2\text{-Tube}}}{\partial r} + \frac{\partial^2 c_{SO_2\text{-Tube}}}{\partial z^2}\right] - U_{\text{Tube}}\frac{\partial c_{SO_2\text{-Tube}}}{\partial z} = 0 \tag{16}$$

$$R_{OH^-} + D_{OH^-\text{-Water}}\left[\frac{\partial^2 c_{OH^-\text{-Tube}}}{\partial r^2} + \frac{1}{r}\frac{\partial c_{OH^-\text{-Tube}}}{\partial r} + \frac{\partial^2 c_{OH^-\text{-Tube}}}{\partial z^2}\right] - U_{\text{Tube}}\frac{\partial c_{OH^-\text{-Tube}}}{\partial z} = 0 \tag{17}$$

For laminar flow, the axial flow velocity distribution in the liquid phase is:

$$U_{\text{Tube}}(r) = 2U_{\text{ave-Tube}}\left[1-\left(\frac{r}{r_{\text{in}}}\right)^2\right] \tag{18}$$

where the average flow rate of liquid at the tube side ($U_{\text{ave-Tube}}$, $m\cdot s^{-1}$) can be calculated according to the following equation:

$$U_{\text{ave-Tube}} = \frac{Q_L}{\pi r_{\text{in}}^2} \tag{19}$$

where Q_L is the liquid volume flow, $m^3\cdot s^{-1}$.

The boundary conditions of the mass transfer equations are presented as follows:

$$r = 0,\quad \frac{\partial c_{SO_2\text{-Tube}}}{\partial r} = 0, \text{ (symmetry)} \tag{20a}$$

$$\frac{\partial c_{OH^-\text{-Tube}}}{\partial r} = 0$$

$$r=r_{in},\ c_{SO_2\text{-Tube}}=c_{SO_2\text{-Membrane}}$$
$$c_{OH^-\text{-Tube}}=c_{OH^-\text{-Membrane}} \tag{20b}$$

$$z=0,\ c_{SO_2\text{-Tube}}=0$$
$$c_{OH^-\text{-Tube}}=0 \tag{20c}$$

2 Reaction equation

The reaction of SO_2 with OH^- is assumed to occur as follows,

$$SO_2 + 2OH^- \longrightarrow SO_3^{2-} + H_2O \qquad k_E = 1.0\times10^6\,m^6\cdot mol^{-2}\cdot s^{-1}$$

Where k_E is the reaction rate constant.

3 Numerical solution

The proposed dimensionless model equations for the shell, membrane and tube sides of the contactor were solved by COMSOL software with a built-in solver and the finite element method (FEM) for numerical solutions of differential equations. Figure 4a and Figure 4b show the simulation results of SO_2 concentration distributions in the membrane contactor in axial and radial directions, respectively, for a MGA test. The SO_2 flux and SO_2 removal efficiency for various membrane properties and operational conditions can be calculated based on the SO_2 concentration variations in the gas and liquid phases.