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Sulfur Dioxide Removal from Flue Gas Using a Molten Salt Membrane

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Abstract: A new method, molten salt membrane, of removing sulfur dioxide from flue gas is proposed in this paper. The rate of mass transfer of SO_2 across the molten salt membrane (MSM) can be explained satisfactorily by the use of non-equlibrium thermodynamics. The mathematical model of SO_2 transfer across MSM is established and calculated by an electronic computer to obtain the solution. The experimental quantities, such as the electric current density, the concentration of SO_2 and the gas flow rate in cathode or anode compartment are tested. The experimental results are in good agreement with the model.

Key words: sulfur dioxide; removal; molten salt membrance

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Introduction

The new technology for gas separation, supported molten salt membrane (MSM) method, has expanded since 1970s on the basis of the supported liquid membrane. Because the stability of liquid membrane is far from satisfactory, Winnick Jack[1~3] adopted the new achievement in fuel cell research, substituted the molten electrolyte for the liquid electrolyte, and developed the supported moltensalt membrane method. Although the method has been used for removing CO_2 from the gases, the research into the sulfur dioxide separation is seldom, especially the mathematical description of mass transfer rate in MSM is as sparse as the morning stars. The purpose of this paper is to establish the mathematical model by using non-equilibrium thermodynamics theory, to calculate the model on an electronic computer and to set up the experimental equipment for testing the effects of various variables on SO_2 transfer rate.

1 Theoretical Analysis

The principle of SO_2 removal using a molten salt membrane is shown in Fig.1[4,5], which involves the use of ternary eutectic mixture of lithium, potassium and sodium sulfates as electrolyte, meta-lithium aluminate as supported material and DC electric field as driving force. The electrodes are made of stainless steel meshes. When the contaminated flue gas is fed to the cathode of the cell, the chemical reaction below occurs[4]

$$SO_2 + O_2 + 2e \rightarrow SO_4^{2-} . \quad (1)$$

Sulfate ions migrate in the applied field to the anode. Where the sulfate ion is oxidized

$$SO_4^{2-} \rightarrow SO_2 + O_2 + 2e . \quad (2)$$

The result is that sulfur dioxide is removed in cathod chamber and recovered in anode chamber.

In this investigation, the experimental conditions are controlled so as to eliminate the diffusion resistance of SO_2 in cathode or anode chamber. In order to establish the mathematical model of the system, the linear non-equilibrium thermodynamics is used, and moreover, some assumptions should be introduced.

First, it is assumed that SO_2 diffusion process is in steady state, in one dimensional and at a constant temperature. Next, the chemical equilibrium exists in any place of the membrane. Finally, Onsager coefficients are constant. Then the model can be developed when the following factors are taken into account:

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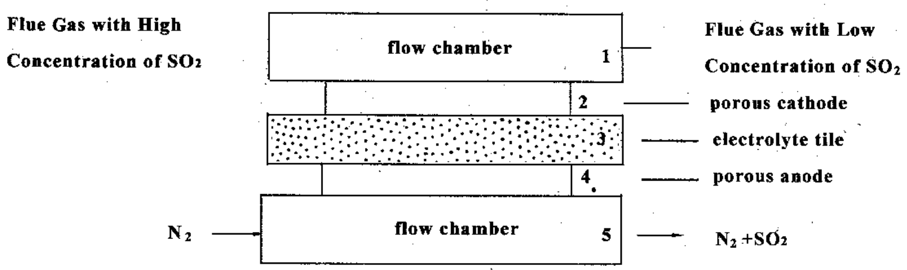
Biography: LIU Jin-dun (1963-), male, born in county Hua, Henan province, professor of Zhengzhou University of Technology, doctor, mainly undertakes the reseach of membrane seperation and industrial gases purification.



1—flow chamber；2—porous cathode；3—electrolyte tile；4—porous anode；5—flow chamber

Fig.1　Sulfur dioxide removal & by using MSM

1.1　The solvent – fixed flux of matter

According to non – equilibrium thermodynamics, the ternary system, containing three cations, 1,2 and 3, and one anion, 0, may be described by the linear relations[6～8]

$$J_0^0 = 0 \,, \tag{3}$$

$$\begin{bmatrix} J_1^0 \\ J_2^0 \\ J_3^0 \end{bmatrix} = \begin{bmatrix} l_{11} & l_{12} & l_{13} \\ l_{21} & l_{22} & l_{23} \\ l_{31} & l_{32} & l_{33} \end{bmatrix} \begin{bmatrix} X_1 \\ X_2 \\ X_3 \end{bmatrix} , \tag{4}$$

Onsager coefficients are found empirically and theoretically to be symmetric

$$l_{ij} = l_{ji} \quad (i \neq j) \,. \tag{5}$$

The one – dimensional case is considered for convenience, and the thermodynamic force can be described as, because this is the usual experimental situation. Here is

$$X_j = -\left(\frac{d\mu_j}{dx} + Z_j F \frac{d\varphi}{dx}\right) \quad (j = 1,2,3) \,; \tag{6}$$

As the flux tested in the experiment is related to the volume – fixed reference frame, according to Prigogine's theory[9], it can be transformed from the solvent – fixed reference frame

$$N_i = J_i^0 + C_i U_c \quad (i = 0,1,2,3) \,. \tag{7}$$

1.2　Chemical reaction in the membrane

In the MSM, the concentration of SO_4^{2-} is higher and it changes so slightly that we can believe that the chemical equilibrium equation below is tenable:

$$K = C_A C_4 \,. \tag{8}$$

1.3　The mass transfer of O_2^{2-}

Mamantov thinks that the concentration of O_2 is less than that of any other ions and Nernst – planck equation can be used to describe its transfer rate[10]

$$D_4\left(\frac{dC_4}{dx} - \frac{2FC_4}{RT}\frac{d\varphi}{dx}\right) \,. \tag{9}$$

1.4　The local electroneutrality in the membrane

Based on electrochemical theory, there is the local electroneutrality at all points in the membrane. So that we can get the equation

$$2C_0 + 2C_4 = C_1 + C_2 + C_3 \,. \tag{10}$$

1.5　The conservation of electric charges

If the used electric current density is I, the conservation equation of electric charges is given by

$$\frac{I}{2F} = N_0 + N_4 \,. \tag{11}$$

1.6　The mass transfer of the cations

Although the cations migrate in the membrane as the carrier or complex, they can not pass through the membrane. For the volume – fixed reference frame, the following equation can be tenable

$$N_i = 0 \quad (i = 1,2,3) \,. \tag{12}$$

1.7　The transfer of SO_2 across the membrane

The total flux of SO_2 across the membrane, which is equal to the flux of sulfur at any points in the membrane, is described by

$$N_A = -D_A \frac{dC_A}{dx} + N_0 \,. \tag{13}$$

Combining equation (3) and (4) with the equation (6 ～ 13), we obtain the mathematical model of SO_2 transfer, that is

$$\left(N_A - \frac{I}{2F}\right) C_A^2 + \left(N_A - \frac{I}{2F}\right)\left(\frac{2KD_4}{\alpha RT}\right) C_A = -\frac{K}{\alpha RT}\left(\frac{I}{F}\right) C_A - D_A C_A^2 \frac{dC_A}{dx} - 2\frac{D_A \cdot D_4 K}{\alpha RT} \cdot C_A \frac{dC_A}{dx} - D_4 K \frac{dC_A}{dx} \,. \tag{14}$$

Where α is the model parameter, $\alpha = f(l_{ij})$.

The boundary conditions are

$$x = 0, \quad C_A = C_{AO} \,; \tag{15}$$

$$x = L, \quad C_A = C_{AL} \,. \tag{16}$$

For the sake of simplicity, the dimensionless variables are introduced $\bar{C}_A = C_A/C^*$; $\bar{x} = x/L$; $\bar{D}_A = D_A/D^*$; $\bar{D}_4 = D_4/D^*$; $\bar{k} = K/(C^*)^2$; $\bar{\alpha} = \alpha RT(C^* \cdot D^*)$; $\bar{N}_A = N_A \cdot L/(C^* \cdot D^*)$; $\bar{I} = (\frac{I}{F})(\frac{I}{C^* \cdot D^*})$, and the model becomes, in dimensionless form,

$$\frac{d\bar{C}_A}{d\bar{x}} = -\frac{(\bar{N}_A - \frac{\bar{I}}{2})(\bar{C}_A^2 + 2\bar{\beta}\bar{C}_A) + \bar{\beta}\bar{I}\bar{C}_A}{\bar{D}_A\bar{C}_A^2 + 2\bar{\beta}\bar{D}_A\bar{C}_A + \bar{\alpha}\bar{\beta}}, \tag{17}$$

where $\bar{\beta} = F(\bar{\alpha})$. with the boundary condition

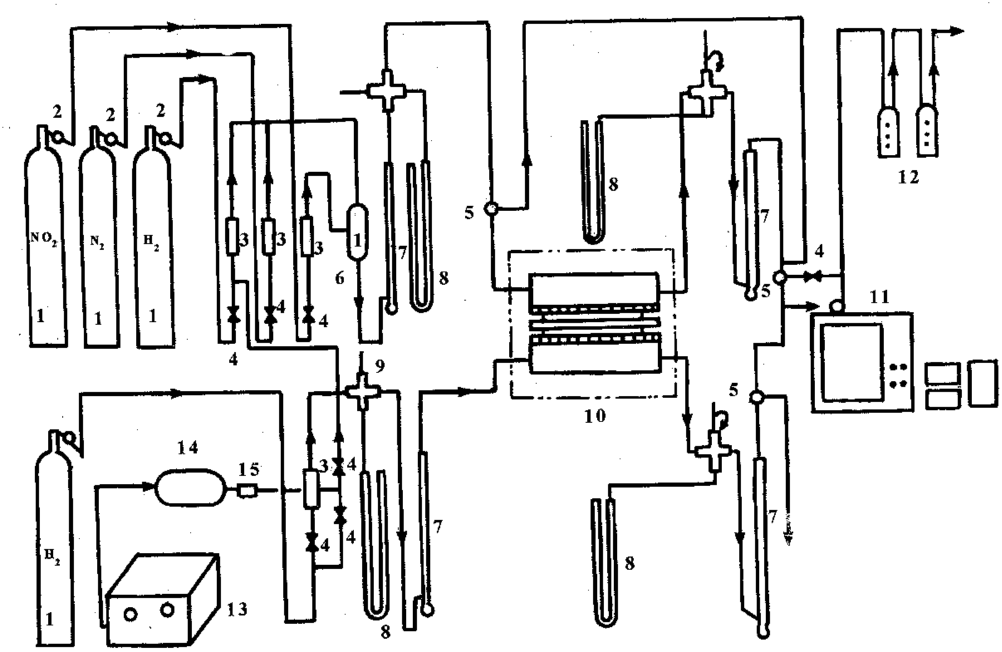
$$\bar{X} = 0,\quad \bar{C}_A = \bar{C}_{AO}; \tag{18}$$

$$\bar{X} = 1,\quad \bar{C}_A = \bar{C}_{AL}. \tag{19}$$

2 Experimental Study

In experimental section, the main equipment is a electrochemical cell, which consists of three parts, that is, the stainless steel housing, the porous electrode and the supported molten electrolyte membrane. Inlet and outlet connections are made to stainless steel tubes which also act as current leads. The tubes are as long as possible so that the gas coming in the cell can reach operating temperature. In molten sulfate membrane, the fused electrolyte, (78.0% Li_2SO_4 + 13.5% K_2SO_4 + 8.5% Na_2SO_4), is contained in the capillary pores of the ceramic tile, that is, $LiAlO_2$. The porous electrodes are held against the electrolyte tile. The experimental flow diagram is shown in Fig.2.

During experiment, the SO_2 coming from the cylinder passes through the needle adjusting valve and mixes with nitrogen and oxygen gases from other cylinders in gas mixer. After the measurement of temperature, pressure, and flow rate, the mixed gas is fed to the cathode of the electrochemical cell. Nitrogen gas or air is fed to the anode of the cell to draw SO_2 migrated from the cathode out. Details of the analysis of SO_2 at the inlet and outlet of the cell are given for calculating its transfer rate.



1—gas cylinder; 2—pressure gauge; 3—rotating flow meter; 4—flow adjusting valve; 5—three way valve; 6—gas mixer; 7—soap flow meter; 8—U pressurer; 9—thermometer; 10—electrochemical cell; 11—gas chromatogramer; 12—absorption bottle; 13—air compressor; 14—buffer tank; 15—air adjusting valve

Fig.2 Sketch of electrochmical removal of SO_2 using MSM

3 Results and Discussion

3.1 Calculation of the model

The model (17) was solved using the Runge – kutta method. In this paper, an IBM computer was programed to give the calculation results. First, the independent experimental quantities, such as the specific conductance, Hittorf transference numbers and the dif

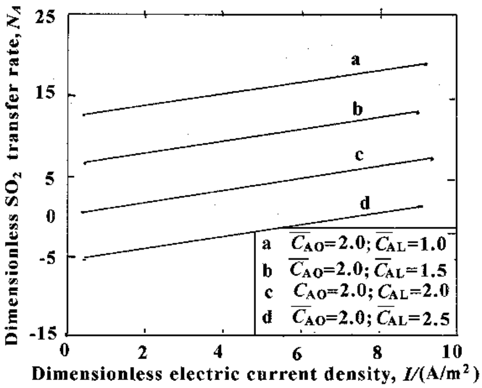


Fig.3　Dimensionless SO_2 transfer rate vs. dimensionless electric current density

– fusion coefficients, were used to obtain Onsager coefficients, as listed in Table 1. Next, the parameters in the model were calculated and also listed in Table 1. Finally, at a specific concentration on two sides the membrane, the relations of SO_2 transfer rate to the electric current density were shown in Fig.3. and Fig.4. It can be seen that SO_2 transfer rate increases with increasing current density and concentration difference. Especially when current density is very small, the effect of concentration difference on SO_2 transfer rate is obviously great, and vice versa.

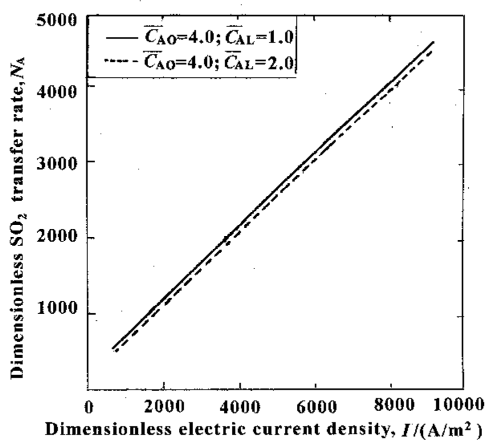


Fig.4　Dimensionless SO_2 transfer rate vs. dimensionless electric current density

Table 1　Onsager coefficients and Parameters for calculation of the model　　mol^2/(J·m)

l_{11}	l_{22}	l_{33}	l_{12}	l_{13}	l_{23}	α	β
2.58×10^{-9}	2.49×10^{-10}	2.50×10^{-10}	2.68×10^{-10}	0.82×10^{-10}	0.08×10^{-10}	1.95×10^{-9}	1.76×10^{-9}

3.2　Experimental results

The electrochemical removal of SO_2 from simulated flue – gas has been tested for a variety of current density and inlet concentration of SO_2 in the gases. The typical relation of SO_2 transfer rate to current density and to the concentration, which is shown in Fig.5, is the same as that in the model calculation. The transfer rate or removal efficiency is in direct proportion to the current density. The reasion is that the rate of reaction (1) between SO_2 and O_2 increases with increasing the current density or the inlet concentration. Fig. 6. shows the calculated and experimental values at a specific concentration of SO_2. It is found that the calculated results can be satisfactorily used to predict the characteristics of the experimental data. The main difference between them is caused by the polarization of the electrode.

4　Conclusion

The non – equilibrium thermodynamics was satisfactorily used in describing the transfer rate of SO_2 across the molten sulfate membrane. It has been shown that the electrochemical removal of SO_2 represents a potentially inexpensive technology. It is applicable not only to coal – burning power plant, but also to any other industry with sulfur dioxide emission problem.

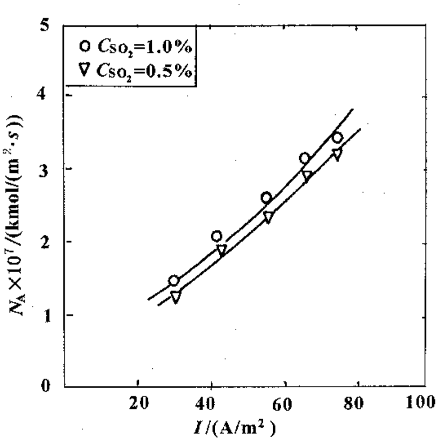


Fig.5　Flux of SO_2 vs. electric current density

Symbles:

A　specie SO_2

C　concentration of specie i

C_i　dimensionless concentration of specie i

I　dimensionless electric current density

J_i　molar flux of specie i, mol/(m^2·s)

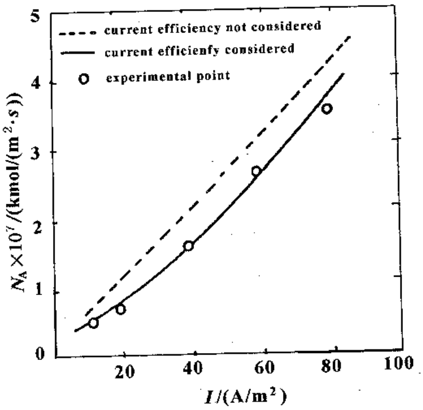


Fig.6 Comparison of experimental results with model calculation date

K chemical equilibrium constant, $[mol/m^3]^2$

L thickness of the membrane, m

l_{ij} Onsager coefficient, $mol^2/(J \cdot m \cdot s)$

N_i mass transfer flux of specie i, $mol/(m^2 \cdot sec)$

N_i mass transfer flux of specie i, $mol/(m^2 \cdot sec)$

U velocity, m/sec

X_i thermodynamic force of specie i, J/mol

x direction of mass transfer

D_i dimensionless diffusion coefficient of specie i

D_i diffusion coefficient of specie i, m^2/sec

F Faraday constant(96500), Columbs/mol

Greek letters

α model parameter

β model parameter

μ_i chemical potential of specie i, J/mol

Φ_i electrical potential of specie i, V

Subscripts

i specie i

o sulfate ion

Superior Letter

o sulfate ion fixed reference fram

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熔融盐膜法脱除烟道气中的二氧化硫

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摘 要:开发了一种烟气中脱除 SO_2 的新方法,即熔盐膜法.采用非平衡态热力学理论有效地描述二氧化硫通过熔盐膜的传质速率,建立了 SO_2 传质的数学模型,并用计算机求取模型的数值解.实验考察了电流密度、SO_2 浓度、阴极室及阳极室气体流量等实验参数对 SO_2 传质的影响.实验结果与理论解吻合良好.

关键词:二氧化硫;脱除;熔盐膜