



# Influence of by-product salts and $\text{Na}_2\text{CO}_3$ contents on gas–liquid mass transfer process in wet desulfurization of water gas

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## Abstract

Among the different methods of  $\text{H}_2\text{S}$  removal, the wet desulfurization is widely used because of its unique advantages. Wet desulfurization usually employs alkaline  $\text{Na}_2\text{CO}_3$ – $\text{NaHCO}_3$  buffer solution as desulfurization agent, which can react with  $\text{H}_2\text{S}$  in absorber tower to produce  $\text{HS}^-$ . Then,  $\text{HS}^-$  is oxidized into sulfur in the presence of a catalyst such as phthalocyanine dicarboxylate sulfonates or other desulfurization catalysts. But unfortunately,  $\text{Na}_2\text{S}_2\text{O}_3$ ,  $\text{Na}_2\text{SO}_3$ ,  $\text{NaSCN}$  and other by-product salts are inevitably generated in the oxidation process. However, the desulfurization pH and the physical properties of the solution such as surface tension, density and viscosity are notably affected by the content in  $\text{Na}_2\text{CO}_3$  and by-product salts. Therefore, it is necessary to investigate the influence of by-product salts and  $\text{Na}_2\text{CO}_3$  on desulfurization efficiency. In this work, the effect of different by-product salts and  $\text{Na}_2\text{CO}_3$  content on the total volumetric mass transfer coefficient  $K_G a$  of  $\text{H}_2\text{S}$  absorption process is experimentally explored. The results revealed that the increase in the by-product salts content results in a decrease in  $K_G a$  and pH values. On the contrary, with the increase in  $\text{Na}_2\text{CO}_3$  content,  $K_G a$  and pH values increased. A mathematical model of the absorption process is proposed and analyzed; the mass transfer coefficient in gas phase  $k_G$  and in liquid phase  $k_L$  as well as secondary reaction constant  $k_2$  is calculated. The results showed that  $K_G a$  was changed mainly by  $k_2$  which reflects the effect of pH. The surface tension, density and viscosity had relatively small effect on  $K_G a$ . The present results provide the required theoretical guidance for practical industrial applications.

**Keywords** By-product salts · Desulfurization · The secondary reaction constant · Mass transfer coefficient

## List of symbols

$a$  Effective mass transfer area per unit volume of packing ( $\text{m}^2/\text{m}^3$ )  
 $a_t$  Surface area per unit volume of packing ( $\text{m}^2/\text{m}^3$ )  
 $C$  Constant  
 $C_{\text{Ai}}$  The concentration of the solute  $\text{H}_2\text{S}$  at the interface ( $\text{kmol}/\text{m}^3$ )  
 $C_{\text{BL}}$  The concentration of the solute  $\text{Na}_2\text{CO}_3$  in the liquid-phase body ( $\text{kmol}/\text{m}^3$ )

$D_G$  Diffusion coefficient in the gas phase ( $\text{m}^2/\text{h}$ )  
 $D_L$  Diffusion coefficient in the liquid phase ( $\text{m}^2/\text{h}$ )  
 $d_p$  Nominal diameter of the packing (m)  
 $G$  Mass velocity of the gas ( $\text{kg}/(\text{m}^2 \text{h})$ )  
 $g$  Gravitational acceleration ( $\text{m}/\text{s}^2$ )  
 $H$  Henry constant ( $\text{kmol}/(\text{m}^3 \text{kPa})$ )  
 $K_G$  Total mass transfer coefficient ( $\text{kmol}/(\text{m}^2 \text{h kPa})$ )  
 $k_G$  Mass transfer coefficient of the gas phase ( $\text{kmol}/(\text{m}^2 \text{h kPa})$ )  
 $k_L$  Mass transfer coefficient of the liquid phase ( $\text{m}/\text{h}$ )  
 $L$  Mass velocity of the liquid ( $\text{kg}/(\text{m}^2 \text{s})$ )  
 $M$  Relative molecular mass ( $\text{kg}/\text{kmol}$ )  
 $N_i$  Mass transfer flux ( $\text{m}^3/\text{h}$ )  
 $P$  Total pressure (kPa)  
 $V_1$  The inert gas velocity in the gas phase ( $\text{kmol}/(\text{m}^2 \text{h})$ )  
 $x_i$  The mole fraction of the component  $i$  in the liquid phase  
 $x_{i,\text{int}}$  The mole fraction of the component  $i$  in the liquid film at gas–liquid interface

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$y_i$	The mole fraction of the component $i$ in the gas phase
$y_i^*$	Equilibrium mole fraction of the component $i$ in the gas phase
$y_{i,int}$	The mole fraction of the component $i$ in the gas film at gas–liquid interface
$y_j$	The mole fraction of the component $j$ in the gas phase
$z$	Packing height (m)
$\sigma$	Liquid surface tension (mN/m)
$\sigma_c$	Critical surface tension of the packing material (mN/m)
$\mu_G$	Gas viscosity (Pa s)
$\mu_L$	Liquid viscosity (Pa s)
$\rho_G$	Gas density ( $\text{kg/m}^3$ )
$\rho_L$	Liquid density ( $\text{kg/m}^3$ )
$\phi_{ij}$	Correlation coefficient between component $i$ and component $j$

## Introduction

The current China concentration standard for  $\text{H}_2\text{S}$  in the air is less than or equal to  $10 \text{ mg/m}^3$  (GBZ of China 2007). In addition, the purification requirements in the oil refinery waste gas call for  $\text{H}_2\text{S}$  concentration in the range of  $10\text{--}20 \text{ mg/m}^3$ .  $\text{H}_2\text{S}$  possesses a serious threat to people's health (Bao et al. 2008). The increase in  $\text{H}_2\text{S}$  concentration in the atmosphere along with the increase in exposure time could result to serious health issues, involving headache, dizziness, nausea, vomiting and even to death depending on its concentration and the duration of exposure. Moreover, serious environmental problems are related with the  $\text{H}_2\text{S}$ , such as acid rain, corrosion of concrete and metals, among others. Zhao et al. (2006) studied the factors affecting the desulfurization in water gas (water gas is produced by the reaction of water vapor with hot anthracite or coke, consisting mainly from hydrogen and carbon monoxide) and semi-water gas (mixture of water gas and air gas) systems. It was revealed that the combustion products and the gas emitted from industrial plants can have significant effects in human health and environment. In addition,  $\text{H}_2\text{S}$  in water gas not only lead to a severe corrosion of equipment, but also to catalyst deactivation in subsequent processes (Wang 2001). Pang et al. (2013) studied the application of MSQ-3 catalyst in the desulfurization of semi-water gas and concluded that the insufficient removal of  $\text{H}_2\text{S}$  could cause a series of problems such as equipment corrosion and catalyst poisoning.

Among the different methods applied for  $\text{H}_2\text{S}$  from water gas, dry desulfurization and wet desulfurization are the most common. Kawase and Otaka (2013) carried out a study on the purification of synthesis gas during biomass gasification by using the molten carbonate method. Yang et al.

(2003) proposed a new method for the absorption of  $\text{CO}_2$  and  $\text{H}_2\text{S}$  by using industrial waste alkaline solutions; the basic parameters affecting  $\text{CO}_2$  and  $\text{H}_2\text{S}$  adsorption were analyzed, and a mass transfer model was established. A wet catalytic oxidation method at room temperature, employing a solution containing ferric, ferrous and cupric ions for  $\text{H}_2\text{S}$  removal, was also investigated (Zhang 2006). Zhang (2005) introduced a method for  $\text{H}_2\text{S}$  removal from coke oven gas by using catalyst composite of phthalocyanine dicarboxylate sulfonates (PDS) and tannin extraction. Wet desulfurization usually employs a desulfurization solution to remove  $\text{H}_2\text{S}$  from water gas by chemical absorption into liquid phase. This method has many advantages such as easy operation, high desulfurization efficiency and low cost, and thus has been widely applied (Yang et al. 2012). The wet flue gas desulfurization (FGD) in the coal-fired power plants is the most widely applied method because of its high  $\text{SO}_2$  removal efficiency, reliability and low utility consumption (Dou et al. 2009). Alkaline  $\text{Na}_2\text{CO}_3\text{--NaHCO}_3$  buffer solution is usually used as a desulfurization solution where the  $\text{H}_2\text{S}$  is reacted with  $\text{OH}^-$  and converted to  $\text{HS}^-$ . The purification efficiency of this particular process, which is usually carried out in an adsorption tower, is largely affected by the pH value of the solution. In order to achieve the required purification efficiency, a careful adjustment of pH range is needed. The solution absorbing  $\text{H}_2\text{S}$  is usually called rich solution, contained in a regeneration tank. In regeneration tank,  $\text{HS}^-$  is oxidized by  $\text{O}_2$  into sulfur in the presence of a desulfurization catalyst such as PDS (Yang et al. 1991) or 888 (an improved desulfurization catalyst based on PDS, which is composed of a trinuclear cobalt phthalocyanine ammonium sulfonate metal organic compound) (Qi et al. 2006). The rich solution without sulfur is called barren solution (Zhang et al. 2015), which is recycled to the absorption tower.

During the oxidization process, side reactions are inevitable and various by-products such as  $\text{Na}_2\text{S}_2\text{O}_3$ ,  $\text{Na}_2\text{SO}_3$ ,  $\text{NaSCN}$  and  $\text{Na}_2\text{SO}_4$  are in addition produced. These by-products have a significant effect on the physical properties of the desulfurization solution and its pH value.  $\text{Na}_2\text{CO}_3$  should be added regularly to the desulfurization solution to maintain a stable pH value (Zhang and Chen 2008). However,  $\text{Na}_2\text{CO}_3$  addition in the desulfurization solution results in an increase in by-product salts, which may lead to salt blockage on the desulfurization tower (Luo and Liu 2006). In addition, the increase in by-product salts can lead to equipment corrosion and to degradation of desulfurization efficiency. In summary, in order to achieve a stable operation of desulfurization process, the pH value of desulfurization solution should be maintained in a specific range (8.60–8.80) and the salts content should be closely monitored (Wang et al. 2007). Extensive research efforts have been put on the absorption of  $\text{H}_2\text{S}$  by alkaline solutions. Different types of absorption liquid, reaction devices and absorption models have been employed toward optimizing

the desulfurization efficiency (Yi et al. 2008). Shang (2012) analyzed the process of H<sub>2</sub>S absorption in a sodium hydroxide solution. Yang et al. (2012) proposed a method of treating acid gas pollution by the absorption of H<sub>2</sub>S with sodium hydroxide solution, and the purified NaHS liquid product was obtained by purification. The process of H<sub>2</sub>S absorption by sodium carbonate solution in a wetted-disk and a wetted-wall column was also proposed and analyzed (Garner et al. 1958). Shimizu et al. (1997) investigated gas and liquid absorption reactions in a wet flue gas desulfurization device. Zhao et al. (2009) used a swirl nozzle and a spiral nozzle in a wet-type desulfurization spray tower under single-layer spray conditions. Bontozoglou and Karabelas (1991) established a numerical model for the simultaneous absorption of CO<sub>2</sub> and H<sub>2</sub>S by NaOH solution, which confirmed the role of CO<sub>2</sub> dissociation in improving the dynamic selectivity of hydrogen sulfide absorption. Wallin and Olausson (1993) established a model for predicting the absorption rate of H<sub>2</sub>S and CO<sub>2</sub> in sodium carbonate solution, exploring the influence of carbonate concentration, gas flow velocity and temperature on the removal efficiency of H<sub>2</sub>S and CO<sub>2</sub>. Park and Kang (1995) developed a new computer program for the simulation of chemical absorption of H<sub>2</sub>S and CO<sub>2</sub> by using a hot potassium carbonate solution, MEA or DEA. Kiil et al. (1998) developed a detailed model for a wet FGD pilot plant based on a packed tower concept and conducted a parameter analysis toward validating assumptions and extracting information on wet FGD systems. However, the influence of by-product salts on the desulfurization efficiency has been rarely investigated. Meng and Li (2010), taking into consideration three parameters (surface tension, density and viscosity) investigated the effect of by-product salts on the desulfurization efficiency of tannin extract desulfurization liquid. Wang et al. (2008) explored only the influence of by-product salts on the density of tannin extract desulfurization liquid. Literature studies on the effect of by-product salts and Na<sub>2</sub>CO<sub>3</sub> on the desulfurization of H<sub>2</sub>S in water gas by using the Na<sub>2</sub>CO<sub>3</sub>–NaHCO<sub>3</sub> buffer solution with PDS as the catalyst are limited.

The objective of this study is to systematically explore how the by-product salts affect the desulfurization efficiency. In this work, the influence of by-product salts and Na<sub>2</sub>CO<sub>3</sub> on the gas–liquid mass transfer in the H<sub>2</sub>S absorption process was investigated by experimental methods. The obtained results can provide valuable insights in relation to the control of by-product concentration and pH values for efficient desulfurization in real practical applications.

## Experimental device and method

Figure 1 schematically illustrates the absorption tower and the setup used in the present study. The tower was filled with Raschig ring packing (material, ceramics;

diameter × height × thickness is 3 mm × 3 mm × 1 mm). The inner diameter of the tower is 25 mm, and the packing layer is 360 mm high. The tower has a circulating warm water jacket to regulate the temperature of H<sub>2</sub>S absorption process. In order to ensure the reliability of the experimental device and the repeatability of the experiment, the necessary verification was carried out before starting the experiment. The average error of verification is lower than 5%. Each sample was analyzed every 30 min, and three measurements were obtained for each sample to take the average.

The desulfurization solution of a certain composition was prepared, and its physical properties such as surface tension (Rotenberg et al. 1983), density, viscosity (Tao et al. 2012) and pH (Yang et al. 2014) were determined. The flow of the desulfurization solution into the absorption tower was measured by a rotor flowmeter; the jacket of the tower was provided with a circulating warm water at 37 °C. The mixture of N<sub>2</sub> and H<sub>2</sub>S was used to simulate the processed gas with H<sub>2</sub>S composition of about 2000 ppm. The mixture gas was measured by rotor flowmeter and went into the tower bottom. The desulfurization solution contacted with the gas during countercurrent movement in the tower to provide the necessary mass transfer for absorption. The intake and exhaust gas samples were taken, and H<sub>2</sub>S content was analyzed by gas chromatography. During the experiment, the gas flow rate was fixed at 180 L/h, while the desulfurization solution flow rate was fixed at 8.4 L/h (Yue et al. 2017).

## Preparation of desulfurization solution

In areal production process, the mass ratio of the by-product salts produced by different raw materials is varied. In this work, the mass ratio used to prepare the desulfurization solution is: M (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>):M (NaSCN):M (Na<sub>2</sub>SO<sub>3</sub>):M (Na<sub>2</sub>SO<sub>4</sub>) = 1:0.110:0.076:0.074, determined via continuous

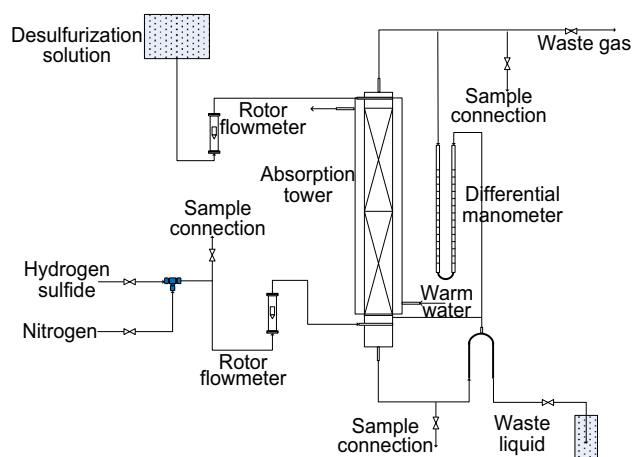


Fig. 1 Scheme of the experimental installation

tracking analysis in a water gas purification device. The content of  $\text{NaHCO}_3$  and desulfurization catalyst PDS in desulfurization solution is constant and equal to 38 and 0.033 g/L, respectively.

### Calculation of the total volumetric mass transfer coefficient $K_G a$

$K_G a$  is an important parameter to characterize gas–liquid mass transfer device. The gas-phase component  $i$  ( $\text{H}_2\text{S}$ ) diffuses from the gas phase to the gas surface and liquid film and then into the liquid phase where it reacts with the absorbent. The mass transfer flux can be expressed as (Treybal 1980):

$$N_i = K_G P (y_i - y_i^*) \quad (1)$$

According to the mass conservation law, for a mass transfer unit at the packing height of  $dz$ , there is a differential equation:

$$\begin{aligned} N_i a dz &= K_G a P (y_i - y_i^*) dz \\ &= -V_1 d\left(\frac{y_i}{1 - y_i}\right). \end{aligned} \quad (2)$$

When the fraction of component  $i$  in gas phase is relatively low,  $y_i/(1 - y_i) \approx y_i$ ,  $V_1 \approx V$ . In this work, the equilibrium partial pressure is relatively small and can be neglected. Thus, formula (2) can be approximately expressed as:

$$-\frac{dy_i}{y_i} = \frac{K_G a P}{V} dz. \quad (3)$$

The definite integral of formula (3) is:

$$-\ln \frac{y_{i,2}}{y_{i,1}} = \frac{K_G a P}{V} z. \quad (4)$$

The total volumetric mass transfer coefficient  $K_G a$  is:

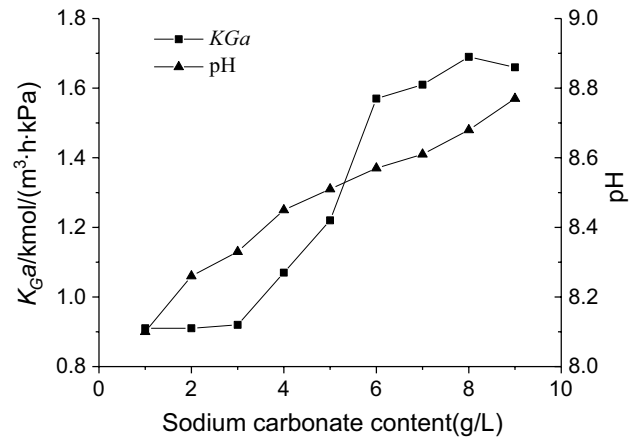
$$K_G a = \frac{V}{Pz} \ln \frac{y_{i,1}}{y_{i,2}}. \quad (5)$$

The effective mass transfer area ( $a$ ) is calculated by formula (6) (Onda et al. 1968):

$$\begin{aligned} a/a_t &= 1 - \exp \\ &\left[ -1.45 \left(\frac{\sigma_c}{\sigma}\right)^{0.75} \left(\frac{L}{a_t \mu_L}\right)^{0.1} \left(\frac{a_t L^2}{\rho_L^2 g}\right)^{-0.05} \left(\frac{L^2}{\rho_L a_t \sigma}\right)^{0.2} \right]. \end{aligned} \quad (6)$$

**Table 1** By-product salts contents in desulfurization solution

$\text{Na}_2\text{S}_2\text{O}_3$ (g L <sup>-1</sup> )	$\text{NaSCN}$ (g L <sup>-1</sup> )	$\text{Na}_2\text{SO}_3$ (g L <sup>-1</sup> )	$\text{Na}_2\text{SO}_4$ (g L <sup>-1</sup> )
51.00	5.63	3.90	3.75
100.00	11.00	7.64	7.35



**Fig. 2** Effects of  $\text{Na}_2\text{CO}_3$  content on pH value and  $K_G a$  ( $\text{Na}_2\text{S}_2\text{O}_3$  content is 51 g/L)

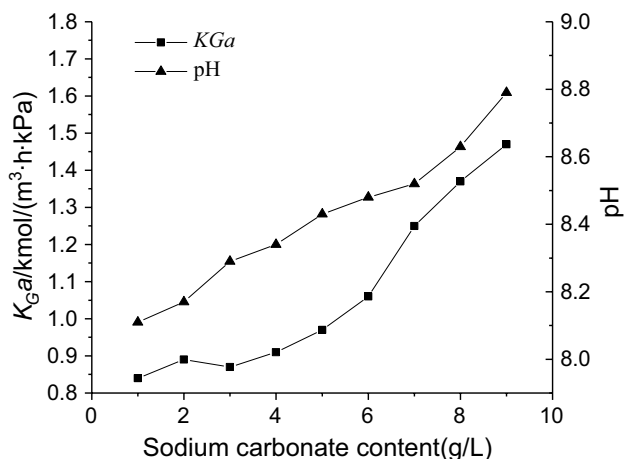
### Effects of various experimental factors on $K_G a$

#### The influence of $\text{Na}_2\text{CO}_3$ content

According to the study of Aleboye et al. (2008), the  $\text{Na}_2\text{CO}_3$  content has a significant effect on  $K_G a$ . Two desulfurization solutions were prepared with different concentration in  $\text{Na}_2\text{CO}_3$  and by-product salts. The  $\text{Na}_2\text{S}_2\text{O}_3$  content in the two different solutions is 51.00 and 100.00 g/L, respectively, whereas the other by-product salts content is proportionally calculated (Yue et al. 2017), as shown in Table 1.

In the as-prepared desulfurization solutions, the  $\text{Na}_2\text{CO}_3$  content was changed in the range of 1–9 g/L, and the corresponding physical parameters of the solution (surface tension, density, viscosity, pH) were measured (Yue et al. 2017). The effect of  $\text{Na}_2\text{CO}_3$  content on absorption (the total volumetric mass transfer coefficient  $K_G a$ ) was experimentally investigated. The results are shown in Figs. 2 and 3.

With the increase in  $\text{Na}_2\text{CO}_3$  content, the pH of the two desulfurization solutions increases almost linearly. The pH value of the solution with lower content in by-product salts is slightly larger at the same  $\text{Na}_2\text{CO}_3$  content, which indicates



**Fig. 3** Effects of Na<sub>2</sub>CO<sub>3</sub> content on pH value and  $K_{Ga}$  (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> content is 100 g/L)

**Table 2** By-product salts contents of desulfurization solution

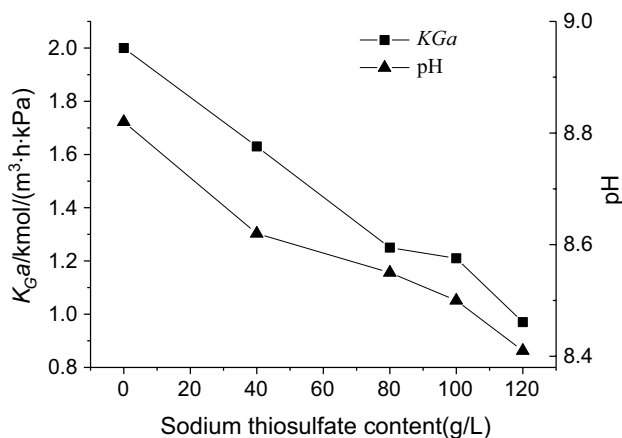
Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> (g L <sup>-1</sup> )	NaSCN (g L <sup>-1</sup> )	Na <sub>2</sub> SO <sub>3</sub> (g L <sup>-1</sup> )	Na <sub>2</sub> SO <sub>4</sub> (g L <sup>-1</sup> )
0	0	0	0
40	4.4	3.04	2.96
80	8.8	6.08	5.92
100	11	7.64	7.35
120	13.2	9.12	8.88

that the increase in the by-product salts content leads to a decrease in the pH value. With the increase in Na<sub>2</sub>CO<sub>3</sub> content,  $K_{Ga}$  significantly increases, following, however, the same trend in the two different solutions. The  $K_{Ga}$  of the solution with lower content in by-products is larger at the same Na<sub>2</sub>CO<sub>3</sub> content, implying that the presence of by-product salts hinders the gas–liquid mass transfer.

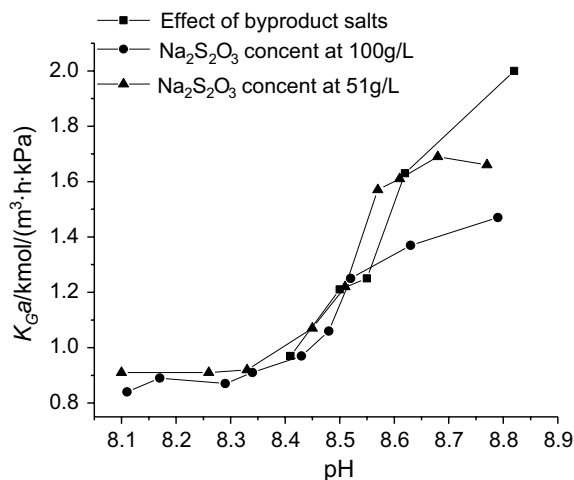
**Effect of by-product salts content**

The Na<sub>2</sub>CO<sub>3</sub> content was fixed at 6 g/L, whereas by-product salts content is changed as shown in Table 2. The effect of by-product salts on pH value and  $K_{Ga}$  was experimentally investigated, and the results are shown in Fig. 4.

It is obvious that both the  $K_{Ga}$  and pH are monotonically decreasing as a function of by-product salts content. In particular, the pH decreased from 8.82 to 8.41 and  $K_{Ga}$  from 2 to 0.97 kmol/(m<sup>3</sup> h kPa) upon increasing by-products content from 0 to 120 g/L, respectively (Fig. 4). The increase in the by-product salts content leads to the change of pH value, density, viscosity and surface tension of the desulfurization solution, which in turn results in an increase in the liquid film resistance accompanied by a substantial reduction of  $K_{Ga}$  (Yue et al. 2017).



**Fig. 4** Effects of by-product salts content on pH value and  $K_{Ga}$



**Fig. 5** Effect of pH value on  $K_{Ga}$

**The effect of pH values**

Figure 5 depicts the influence of pH on  $K_{Ga}$ , under different by-product salts content.

It is evident that  $K_{Ga}$  slightly changes when the pH varies from 8.1 to about 8.4. However, for pH values higher than 8.4 the  $K_{Ga}$  is increased rapidly in all cases. According to Fig. 5, the pH value of desulfurization solution should be kept more than 8.65 to maintain a higher and more stable absorption effect. Figure 5 also depicts the influence of the by-product salts content on  $K_{Ga}$  under the same pH value, which is induced by the different physical properties of the desulfurization solution. In general, at the same pH, higher  $K_{Ga}$  values are obtained for lower by-product salts content. It is also of worth noticing that the influence of by-products content on  $K_{Ga}$  is strongly depended on pH values, being more intense for values higher than 8.5. It is considered that two main factors affect the mass transfer process during desulfurization. The first one is



the pH of the solution, which affects the chemical adsorption. The second one is the by-product salts content, which alters the physical properties of the desulfurization solution. The impact of these particular parameters on mass transfer coefficient is analyzed in the following section.

### Mass transfer coefficient

In the gas–liquid mass transfer processes,  $H_2S$  transferred into the solution through the gas-phase and liquid-phase boundary resistance layers. The mass transfer flux can be expressed as:

$$N_i = k_G P(y_i - y_{i,int}) = Hk_L(x_{i,int} - x_i) = K_G P(y_i - y_i^*) \quad (7)$$

The total mass transfer resistance is the sum of the liquid-phase boundary resistance and the gas-phase boundary resistance. For chemical absorption, the enhancement factor  $E$  is used to represent the influence of chemical reaction on the total mass transfer coefficient.  $K_G$ ,  $k_L$  and  $k_G$  are related through the equation:

$$\frac{1}{K_G} = \frac{1}{k_G} + \frac{1}{HEk_L} \quad (8)$$

$k_L$  and  $k_G$  are computed by using the correlation proposed by Onda et al. (1968):

$$k_L = 0.051 \left( \frac{L}{a\mu_L} \right)^{2/3} \left( \frac{\mu_L}{\rho_L D_L} \right)^{-1/2} \left( \frac{\rho_L}{\mu_L g} \right)^{-1/3} (a_t d_p) \quad (9)$$

$$k_G = \frac{CG}{MP} \left( \frac{Gd_p}{\mu_G} \right)^{-0.3} \left( \frac{\mu_G}{\rho_G D_G} \right)^{-2/3} (a_t d_p)^{-2/3} \quad (10)$$

$$\mu_G = \frac{\sum_{i=1}^n y_i \mu_i}{\sum_{j=1}^n y_j \phi_{ij}} \quad (11)$$

The enhancement factor  $E$  (Shi et al. 1996) is calculated as follows:

$$E = \frac{Ha[(E_i - E)/(E_i - 1)]^{1/2}}{\tanh \left\{ Ha[(E_i - E)/(E_i - 1)]^{1/2} \right\}} \quad (12)$$

$E_i$  is the enhancement factor of the instantaneous reaction (Shi et al. 1996):

$$E_i = 1 + \frac{D_B C_{BL}}{D_L C_{Ai}} \quad (13)$$

In Eq. (12),  $Ha$  is Hatta number, calculated by the following equation (Shi et al. 1996):

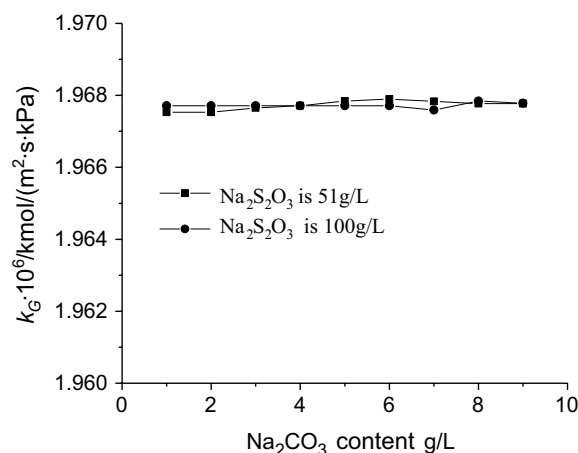


Fig. 6 Effect of  $Na_2CO_3$  content on  $k_G$

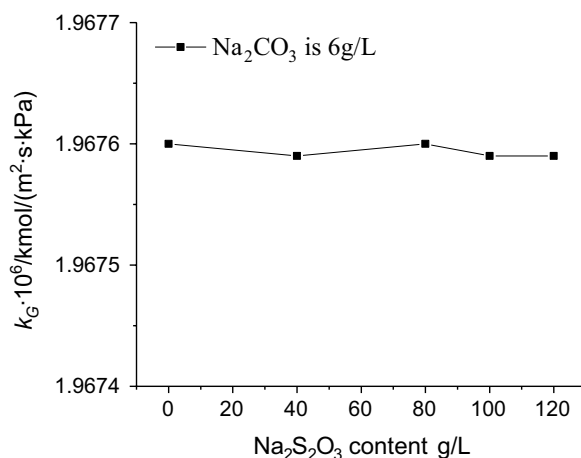


Fig. 7 Effect of by-product salts content on  $k_G$

$$Ha = \sqrt{D_L k_2 C_{BL}} / k_L \quad (14)$$

The  $k_2$  in Eq. (14) is the rate constant of a second-order reaction.

### Effect of $Na_2CO_3$ and by-product salts on $k_G$ and $k_L$

According to the physical properties data and the experimental absorption parameters such as gas and liquid phase flow, the  $k_G$  and  $k_L$  of  $H_2S$  absorption process can be calculated by Eqs. (9) and (10). The influence of  $Na_2CO_3$  and by-product salts content on  $k_G$  is shown in Figs. 6 and 7, respectively. The  $k_G$  value remains constant, indicating that the composition of the desulfurization solution does not affect  $k_G$ .

Figure 8 depicts the influence of  $Na_2CO_3$  content on  $k_L$  for the two different solutions (51 and 100 g/L  $Na_2S_2O_3$ ). A similar trend is observed in both solutions;  $k_L$  is gradually decreased with the increase in  $Na_2CO_3$  content. Figure 9

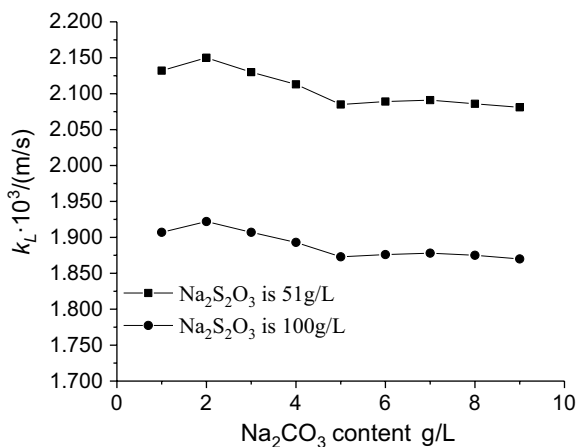


Fig. 8 Effect of Na<sub>2</sub>CO<sub>3</sub> content on *k<sub>L</sub>*

shows the influence of the by-product salts content on *k<sub>L</sub>* when the Na<sub>2</sub>CO<sub>3</sub> content is fixed. The *k<sub>L</sub>* is decreased linearly upon increasing the by-product salts content. It can be therefore argued that both the Na<sub>2</sub>CO<sub>3</sub> and by-product salts content can alter the properties of the desulfurization solution and in turn the *k<sub>L</sub>*.

### The influence of pH value on the enhancement factor E

As shown in Fig. 8, the results reveal that the physical properties of the solution can affect the *k<sub>L</sub>* (and thus *K<sub>G</sub>a*). However, the enhancement factor *E* which reflects the effect of chemical reaction on the absorption process is not included in *k<sub>L</sub>*. The effect of chemical reaction is essentially manifested by the constant rate *k<sub>2</sub>* of the second-order reaction in formula (14).

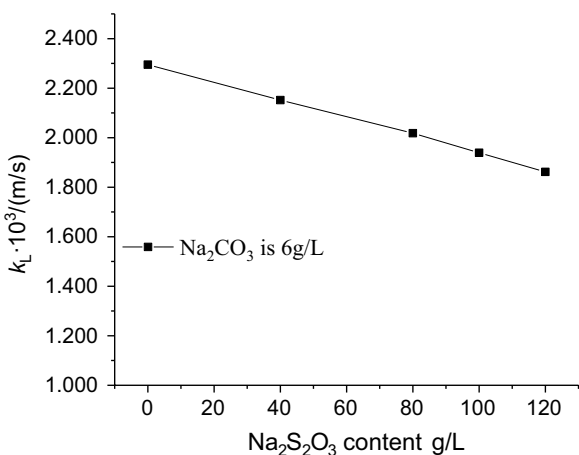


Fig. 9 Effect of by-product salts content on *k<sub>L</sub>*

According to Eqs. (8)–(14) and the *K<sub>G</sub>a* values determined experimentally, the corresponding *k<sub>2</sub>* values in H<sub>2</sub>S absorption process can be calculated (Table 3). It can be seen that the variation trend of *k<sub>2</sub>* is basically the same as that of *K<sub>G</sub>a*. Therefore, compared with *k<sub>L</sub>* and *k<sub>G</sub>*, the chemical reaction enhancement factor *E* is the main factor affecting *K<sub>G</sub>a*. When the pH value is less than 8.52, the *k<sub>2</sub>* of the different desulfurization solutions is basically the same. In contrast, when the pH value is larger than 8.52, the *k<sub>2</sub>* is strongly depended on the content of desulfurization solution in by-product salts.

### Conclusion

In this work, the influence of by-product salts on desulfurization efficiency was investigated. The results showed by changing Na<sub>2</sub>CO<sub>3</sub> and by-product salts content, the physical properties (density, viscosity and surface tension) and the pH of desulfurization solution are notably altered, which in turn affects the total volumetric mass transfer coefficient *K<sub>G</sub>a* in the H<sub>2</sub>S absorption process. Compared

Table 3 *k<sub>2</sub>* of different solutions at the same pH value

Solution pH value	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> is 51 g/L <i>k<sub>2</sub></i> × 10 <sup>5</sup> /m <sup>3</sup> /kmol s	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> is 100 g/L <i>k<sub>2</sub></i> × 10 <sup>5</sup> /m <sup>3</sup> /kmol s	Na <sub>2</sub> CO <sub>3</sub> is 6 g/L <i>k<sub>2</sub></i> × 10 <sup>5</sup> /m <sup>3</sup> /kmol s
8.10	0.51	–	–
8.11	0.51	0.52	–
8.17	0.77	0.76	–
8.26	1.60	1.60	–
8.29	2.16	2.18	–
8.33	2.22	2.23	–
8.34	2.24	2.23	–
8.41	2.28	2.27	2.27
8.43	2.29	2.29	2.28
8.45	2.32	2.33	2.32
8.48	2.42	2.40	2.42
8.50	3.39	3.38	3.39
8.51	3.52	3.49	3.51
8.52	3.59	3.55	3.58
8.55	13.06	3.63	3.61
8.57	22.40	3.69	11.41
8.61	22.48	3.77	22.39
8.62	22.52	3.85	22.53
8.63	22.59	3.93	22.62
8.68	22.85	4.25	23.09
8.77	22.78	4.89	24.84
8.79	–	5.03	25.12

with the physical properties of the desulfurization solution, pH has a greater effect on  $K_G a$ .

The results also showed that the composition of the desulfurization solution does not affect  $k_G$ , whereas  $\text{Na}_2\text{CO}_3$  and by-product salts content has no significant effect in  $k_L$ . Upon increasing the pH, the constant rate  $k_2$  representing the chemical absorption is changed accordingly to  $K_G a$ , implying that the mass transfer coefficient is mainly affected by the  $k_2$ . Therefore, compared with  $k_L$  and  $k_G$ , the chemical reaction enhancement factor E is the main factor affecting  $K_G a$ .

The effective control of the  $\text{H}_2\text{S}$  content in the air is of major importance toward improving air quality, preventing ecological damage and protecting human health. The results of this study can provide valuable insights for the effective control of  $\text{H}_2\text{S}$  in practical industrial applications. The work for removal of  $\text{H}_2\text{S}$  can effectively avoid and solve the potential environmental problems.

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