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Kinetic study of hydrogen sulfide absorption in aqueous chlorine solution

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ABSTRACT

Hydrogen sulfide (H_2S) is currently removed from gaseous effluents by chemical scrubbing using water. Chlorine is a top-grade oxidant, reacting with H_2S with a fast kinetic rate and enhancing its mass transfer rate. To design, optimize and scale-up scrubbers, knowledge of the reaction kinetics and mechanism is requested. This study investigates the H_2S oxidation rate by reactive absorption in a mechanically agitated gas–liquid reactor. Mass transfer (gas and liquid sides mass transfer coefficients) and hydrodynamic (interfacial area) performances of the gas–liquid reactor were measured using appropriated physical or chemical absorption methods. The accuracy of these parameters was checked by modeling the H_2S absorption in water without oxidant. A sensitivity analysis confirmed the robustness of the model. Finally, reactive absorption of H_2S in chlorine solution for acidic or circumneutral pH allowed to investigate the kinetics of reaction. The overall oxidation mechanism could be described assuming that H_2S is oxidized irreversibly by both hypochlorite anion ClO^- ($k = 6.75 \times 10^6\ \mathrm{L\,mol^{-1}\,s^{-1}}$) and hypochlorous acid ClOH ($k = 1.62 \times 10^5\ \mathrm{L\,mol^{-1}\,s^{-1}}$).

Keywords: Hydrogen sulfide; Chlorine; Kinetics; Mass transfer; Absorption; Scrubber

1. Introduction

Hydrogen sulfide (H_2S) is a major toxic compound involved in odor emissions of many industries such as waste water treatment, pulp industry, etc. (Gostelow et al., 2001; Kangas et al., 1984; Rappert and Müller, 2005). Proving high and reliable efficiency, chemical wet scrubbing is the most widely used process to prevent H_2S emissions (Busca and Chiara, 2003; Smet and Langenhove, 1998; Smet et al., 1998). This technique involves H_2S mass transfer in an aqueous phase using a gas–liquid contactor. Since H_2S is poorly soluble in water, to increase its removal efficiency, aqueous oxidant solutions at basic pH are often used (Biard et al., 2009; Bonnin, 1991; Chen et al., 2001; Kerc and Olmez, 2010; Le Sauze et al., 1991). Other processes are currently used to remove H_2S: biofiltration, absorption in alkanolamine solutions, absorption using the Claus process or catalysts to recover the elemental sulfur, etc. (Busca and Chiara, 2003; Kohl and Nielsen, 1997).

Due to a strong reactivity with H_2S, chlorine is a top-grade oxidant for this application and is currently used, especially in waste water treatment plants, in rendering and composting facilities, etc. The process is operated semi-continuously (Biard et al., 2010). The scrubbing liquid is stored in a tank located at the bottom of the scrubber and is recirculated. pH and chlorine concentration are regulated. This scrubbing liquid is just drained when the salt accumulation due to H_2S oxidation into sulfate anions becomes too high.

Chlorine speciation in water is rather complex. Depending on the pH, the ionic strength and the chloride concentration, chlorine can be present in water mainly as aqueous chlorine Cl_2, hypochlorous acid ClOH and hypochlorite ions ClO^- (Deborde and Von Gunten, 2008):

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$$Cl_2 + H_2O \rightleftarrows ClOH + H^+ + Cl^- \quad (1)$$

$$K_{Cl_2} = \frac{[ClOH][H^+][Cl^-]}{[Cl_2]} = 3.8 \times 10^{-4} mol^2 L^{-2}$$
$$\text{at 293 K and a negligible ionic strength} \quad (2)$$

$$ClOH \rightleftarrows ClO^- + H^+ \quad K_{A,1} = \frac{[ClO^-][H^+]}{[ClOH]} \text{ with } pK_{A,1} = 7.58$$
$$\text{at 293 K} \quad (3)$$

Cl_2 exists only at acidic pH (<5–6) and its coexistence domain increases with the total chloride concentration. Some additional species such as $Cl_3{}^-$ or Cl_2O can be observed. However, at a low chloride concentration, they can be neglected (Deborde and Von Gunten, 2008). With a higher oxidation potential, ClOH currently reacts faster than ClO^-. These observations emphasize that oxidation kinetics with chlorine are pH dependant.

An excess of chlorine (at least 4 mol of chlorine for 1 mol of H_2S) can mineralize H_2S (oxidation number = −2) in sulfate ion (oxidation number = +6) according to the following global mechanism at alkaline pH:

$$H_2S + 4NaOCl + 2NaOH \xrightarrow{\text{complete oxidation}} Na_2SO_4 + 4NaCl + 2H_2O \quad (4)$$

The first by-product formed after H_2S oxidation is elemental sulfur which can be further oxidized in sulfite $SO_3{}^{2-}$ and sulfate $SO_4{}^{2-}$ (Choppin and Faulkenberry, 1937). In the whole process, oxidation of elemental sulfur into sulfite is considered as the rate limiting step, especially at pH close to the neutrality where colloidal sulfur accumulation can be observed in chemical scrubbing processes (Biard et al., 2009; Bonnin, 1991).

H_2S is a weak diacid in equilibrium with its conjugated base, the hydrosulfide anion HS^- ($pK_{A,2} = 7.07$ at 293° K (Roustan, 2003). The sulfide anion S^{2-} is present only at very basic pH and can be neglected ($pK_{A,3} \approx 17$ at 293° K) at pH used in chemical scrubbing ($pH \leq 11–12$). During H_2S chemical scrubbing in chlorine solutions, both H_2S dissociation in HS^- and oxidation decrease the H_2S bulk concentration, which maintains a maximal and constant mass transfer driving force. Moreover, since the kinetics of these reactions are really fast, mass transfer enhancement is currently observed, which leads to a large removal efficiency (Biard et al., 2010). Indeed, mass transfer enhancement due to these reactions enhances the absorption rate by decreasing the mass transfer resistance in the liquid film (Roustan, 2003). By this way, the whole resistance could be located in the gas phase. Mass transfer enhancement calculation is rather complicated and depends on several parameters: nature (reversible, irreversible) and number of reactions involved, reaction(s) kinetics, reaction(s) stoichiometry, concentrations and diffusion coefficients (van Swaaij and Versteeg, 1992).

Within the current operating conditions, which insure an excess of chlorine (several hundred $mg\,L^{-1}$ are usually set), H_2S and HS^- cannot be measured in the liquid bulk since they are quickly oxidized in the liquid film at the vicinity of the gas–liquid interface. From wet scrubbing experiments in packed column, Bonnin (1991) determined an apparent kinetic constant between H_2S and ClOH of $1.8 \times 10^8\ L\,mol^{-1}\,s^{-1}$ for pH ranging from 9 to 11 at 293 K. However, this determination was based on wrong assumptions (Biard et al., 2010). Therefore, the kinetic rate of H_2S oxidation by chlorine is poorly known whereas it would enable better gas–liquid contactor scale-up, design and optimization.

To answer to this issue, the purpose of this study is to determine the H_2S oxidation kinetics at 293 K with ClOH and ClO^-. Only a few techniques, like stopped flow or competitive methods or reactive absorption, can be used to determine high kinetic constants (Beltrán, 2004). In this particular case, reactive absorption seems to be appropriated (Vaidya and Kenig, 2007b). This technique has been successfully applied in the past to determine kinetic constants in the fields of ozonation, chlorine hydrolysis, flue desulfurization or CO_2 capture in amine solutions (Aieta and Roberts, 1986; Beltrán, 2004; Ebrahimi et al., 2003; Jia et al., 2010; Jing et al., 2012; Kucka et al., 2002; Sema et al., 2012; Sotelo et al., 1991; Vaidya and Kenig, 2007a, 2009).

During H_2S absorption, H_2S removal efficiency is governed by the mass transfer rate which depends on the hydrodynamic and mass transfer performances of the reactor, gas and liquid flow patterns and H_2S oxidation kinetic rate. If all these parameters are controlled, the kinetics can be investigated. To simplify the liquid flow pattern and to insure a homogeneous liquid phase, a gas–liquid contactor agitated by a Rushton turbine has been selected. First of all, the mass transfer and hydrodynamic parameters of the laboratory tank must be determined in controlled conditions (gas and liquid flow rates, pressure, rotation speed). These parameters are determined by physical absorption of oxygen and by chemical absorption of ozone and H_2S in specific mass transfer regimes. Then, the kinetic constant at 293 K can be deduced during H_2S absorption in chlorine solutions set at various concentrations and pH. Chlorine concentration must be optimized to find a compromise between a too low kinetic rate on the one hand and a too large kinetic rate on the other hand to enable an accurate enhancement factor determination. pH will be in the range 5–7.5 to assess the influence of the chlorine speciation and to limit the potential HS^- formation. The next section reviews the mass transfer theory which is required for the gas–liquid contactor characterization and the kinetic constant determination.

2. Mass transfer modeling

Gas–liquid mass transfer can be described according to various theories. Usually, the double film theory (explicative scheme in the supplementary material) is applied in steady state (Whitman, 1923). The molar flux transferred of any species A (dJ in $mol\,m^{-2}\,s^{-1}$) per square meter of gas–liquid area can be written (Perry and Green, 1997):

$$dJ = Ek_L(C_A^* - C_A) = K_L(C_A^{Eq} - C_A) \quad (5)$$

E is the so-called enhancement factor (no unit) which is the ratio of the absorption rate with and without the reaction for an identical difference $C_A^* - C_A$. Other definitions of the enhancement factor can be found in the literature. However, this one remains the most encountered. C_A, C_A^*, C_A^{Eq} are the solute concentration respectively in the bulk ($mol\,m^{-3}$), at the gas–liquid interface (superscript *) and in equilibrium