Modeling Oxidizing Scrubbers for Odor Control

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In an oxidizing scrubber for odor control, the odorant is absorbed in a scrubber and must be oxidized to allow steady-state operation. The rate of absorption depends on the Henry's law coefficient, the gas- and liquid-phase mass transfer coefficients, and the rate of the oxidation reaction. The effect of a liquid-phase reaction on the liquid-phase mass transfer is often expressed in terms of an enhancement factor. Pseudo-first-order reaction rates were estimated for chlorination reactions for selected odorants. For simple amines and ammonia, the pseudo-first-order reaction rate is very fast, resulting in high enhancement factors for typical values of the mass transfer coefficients and odorant liquid-phase diffusion coefficients. For phenol and toluene, the reaction rate is relatively slow, and the enhancement factor is very close to unity.

Introduction

Oxidizing scrubbers can often treat low concentrations of odorants. In a scrubber, the odorant is absorbed in a liquid, which is usually water. In most cases, a chemical reagent in the water neutralizes, oxidizes, or reduces the odorant. Continuous or periodic addition of the reagent allows near steady-state operation of the scrubber system with minimal makeup water supply and blowdown discharge of the scrubbing solution.

The literature on oxidizing scrubbers emphasizes the pragmatic aspects and the effectiveness of various reagents on specific odorants (*1−3*). Oxidants recommended for various odorants include chlorine, sodium hypochlorite, calcium hypochlorite, hydrogen peroxide, ozone, and potassium permanganate.

This paper focuses on modeling aspects of oxidizing scrubbers including the mass transfer coefficients, chemical enhancement of the rate of mass transfer, and the Henry's law coefficient of the odorant. The oxidation reaction is assumed to take place in the liquid.

Theory

The rate of transfer from the gas phase to the liquid phase depends, in part, on the individual gas-phase mass transfer coefficient, k_G, the individual liquid-phase mass transfer coefficient without chemical reaction, k_L^0, and the interfacial area of the contactor, a. Table 1 gives typical values of these coefficients for countercurrent packed columns, sieve tray columns, and spray columns (*4*).

The dimensionless Henry's law coefficient, H, expresses the ratio of the equilibrium concentration in the gas phase to the concentration in the liquid phase:

$$c_G = Hc_L \tag{1}$$

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TABLE 1. Typical Mass Transfer Coefficients and Interfacial Areas for Scrubbers[a]

scrubber	k_G (cm/s)	k_L^0 (cm/s)	a (m²/m³)
countercurrent packed	0.075–5.0	0.004–0.02	10–350
bubble cap tray	1.25–5.0	0.01–0.05	100–400
sieve tray	1.25–15.0	0.01–0.2	100–200
spray tower	1.25–5.0	0.0007–0.015	10–100

[a] Ref 4.

where c_G is the mass concentration in the gas phase, c_L is the mass concentration in the liquid phase, and H is the dimensionless Henry's law coefficient.

Chemical reactions in the liquid phase decrease the liquid-phase concentration and enhance the overall rate of absorption (*5−7*). Depending on the rate of reaction, the reaction may occur at the gas−liquid interface, in the liquid film, or in the bulk liquid. For typical air pollution scrubbing systems, the bulk liquid includes not only the liquid holdup in the absorber but also liquid in the sump and the recirculation lines.

Many liquid-phase oxidation reactions are first order in both the oxidant and the reductant. If the oxidant is present at sufficiently high concentration, the reaction is pseudo-first-order with respect to the odorant. In that case, an enhancement factor can account for the effect of the chemical reaction on the magnitude of the individual liquid-phase reaction coefficient. This first-order enhancement factor is

$$E_1 = \left[1 + \frac{D_L k_1}{(k_L^0)^2}\right]^{1/2} \tag{2}$$

where E_1 is the enhancement coefficient for a first-order reaction, D_L is the liquid-phase diffusion coefficient of the pollutant, and k_1 is the pseudo-first-order reaction coefficient (*7*). This can also be written in terms of the ratio of the diffusion time, t_D, to the reaction time, t_R (*6*):

$$E_1 = \left[1 + \frac{t_D}{t_R}\right]^{1/2} \tag{3}$$

The diffusion time is the characteristic time for the odorant to diffuse through the liquid film, $D_L (k_L^0)^{-2}$. The reaction time is the characteristic time for the reaction to go completion, $(k_1)^{-1}$.

The individual liquid-phase mass transfer coefficient with chemical reaction is

$$k_L = E_1 k_L^0 \tag{4}$$

The overall mass transfer coefficient based on the gas phase, K_G, is

$$K_G = \frac{k_G}{\left[1 + \dfrac{H k_G}{E k_L^0}\right]} \tag{5}$$

In the field of odor control, the rates of reaction have not been considered quantitatively. Fortunately, some liquid-phase reaction rates for the chlorination of odorants have been reported in the field of water and wastewater treatment (*8, 9*).

Results and Discussion

Table 2 gives the dimensionless Henry's law coefficient (*10−12*), the odor threshold for selected odorants (*13, 14*), the

TABLE 2. Estimated Enhancement Factors at 25 °C for Selected Odorants

odorant	CAS No.	H (−)	odor threshold (ppm$_v$)	2nd order rate[a] (L mol^{-1} s^{-1})	k_1[b] (s^{-1})	D_L (m^2 s^{-1})	E[c] (−)
hydrogen sulfide	7783-06-4	0.40	0.00047	NA[d]	very rapid	2.0×10^{-9}	$\gg 1$
ammonia	7664-41-7	0.0007	46.8	4×10^4	4×10^4	2.5×10^{-9}	20
methylamine	74-89-5	0.00045	0.02	3.2×10^8	3.2×10^6	1.6×10^{-9}	144
dimethylamine	124-40-3	0.0007	0.047	1.6×10^8	1.6×10^6	1.3×10^{-9}	93
diethylamine	109-89-7	0.00105	0.02	7.2×10^7	7.2×10^5	1.0×10^{-9}	54
phenol (pH = 8.5)	108-95-2	0.000016	0.047	6.1×10^3	1.02	1.2×10^{-9}	1.002
toluene	108-88-3	0.24	2.14	NA	slow	9.6×10^{-10}	≈ 1

[a] Second-order rate constants based on refs 8 and 9. [b] The pseudo-first-order rate constants based on an HOCl concentration of 0.01 mol/L. [c] Based on an odorant liquid-phase diffusion coefficient estimated using the Wilke−Chang equation, individual gas-phase mass transfer coefficient of 0.05 m/s, and an individual liquid-phase mass transfer coefficient of 0.0005 m/s. [d] Not available.
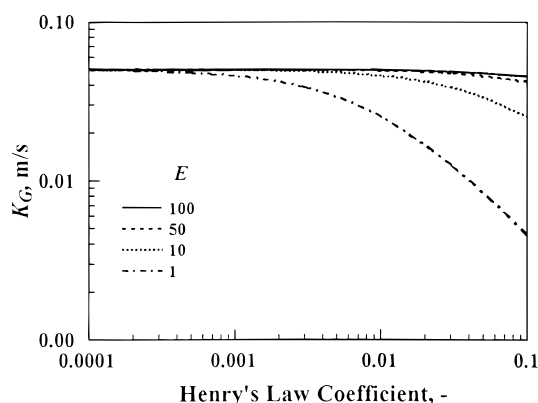

FIGURE 1. Effect of the enhancement factor and Henry's law coefficient on the overall gas-phase mass transfer coefficient, K_G, for $k_G = 0.05$ m/s and $k_L^0 = 0.0005$ m/s.

second-order reaction rates (8, 9), the pseudo-first-order rate, the liquid-phase diffusivity, and the estimated enhancement factor for selected odorants. For the example calculations, the pseudo-first-order reaction rate has been calculated for the HOCl concentration of 0.01 M, which is a mass concentration of 525 mg/L. Although the second-order rate for hydrogen sulfide and toluene are not available, the pseudo-first-order rate has been described as very fast and slow, respectively (9). The liquid-phase diffusion coefficient of the odorant was estimate using the Wilke−Chang equation (15).

The estimated enhancement factor for selected odorants varies from over 140 for methylamine to nearly unity for phenol. Most likely, the enhancement factor for hydrogen sulfide is of the same order of magnitude as those for the amines, and the value for toluene is close to unity.

Figure 1 gives estimates of the overall gas-phase mass transfer coefficient as a function of the Henry's law coefficient and the enhancement factor for typical values of the mass transfer coefficients. When H is very low, such as the case for phenol, the overall gas-phase mass transfer coefficient is nearly equal to the individual gas-phase mass transfer coefficient, which is its upper bound. For this case of low H, a large enhancement factor has no effect on the overall mass transfer coefficient.

When the Henry's law coefficient is large, the enhancement factor can dramatically increase the overall mass transfer coefficient. For example, consider $H = 0.1$, which is slightly less than the value for toluene. For $E = 1$, the overall mass transfer coefficient based on the gas phase is an order of magnitude less than the individual gas-phase mass transfer coefficient. For $E = 10$, the overall mass transfer coefficient is about a factor of 2 less than the individual gas-phase coefficient. For $E = 100$, the overall coefficient almost equals to the individual gas-phase mass transfer coefficient.

Therefore, in this case, a high enhancement coefficient can dramatically improve the rate of absorption.

When the enhancement factor is large, residence time within the film is sufficient to oxidize the odorant. Then the bulk liquid-phase concentration of the odorant in the absorber will be very small. When the enhancement factor is close to unity, the reaction occurs primarily in the bulk liquid. If the characteristic reaction time is long as compared to the actual liquid residence time in the absorber, the reaction will not proceed very far within the absorber, which essentially acts as a physical absorber. If such a system operates at steady state, there must be sufficient liquid residence time in the sump to oxidize the odorant before liquid recycle.

These concepts in modeling should be extended by developing an integrated mathematical model that considers the rates of both mass transfer and chemical reaction. Predictions using this model should be compared to actual data. Application of these concepts may require additional reaction rate coefficients for specific odorants and oxidants.

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