Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Roy, Sharmistha and Rochelle, Gary T.(2004) 'Chlorine Absorption in Sulfite Solutions', Separation Science and Technology, 39: 13, 3057 — 3077
To link to this Article: DOI: 10.1081/SS-200030337
URL: http://dx.doi.org/10.1081/SS-200030337

SEPARATION SCIENCE AND TECHNOLOGY
Vol. 39, No. 13, pp. 3057–3077, 2004

Chlorine Absorption in Sulfite Solutions

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ABSTRACT

The rate of chlorine (5 to 300 ppm Cl_2) absorption into aqueous sulfite/bisulfite (0 to 10 mM S(IV)) was measured using a stirred-cell reactor and a wetted-wall column at pH 4.7 and 5.7. Chlorine absorption was modeled using the theory of mass transfer with fast reaction. Chlorine reacts quickly with S(IV) to form chloride and sulfate near the gas/liquid interface. The rate constant for the reaction of chlorine with S(IV) at 25°C was determined to be 1.1×10^9 L/mol-s. The enhancement of the succinate buffer on the chlorine hydrolysis rate was quantified. The addition of sodium chloride (NaCl) did not affect the rate of Cl_2 absorption in S(IV). Oxygen did not affect the rate of chlorine absorption or catalyze S(IV) oxidation. These results are relevant in the simultaneous removal of chlorine, sulfur dioxide, and elemental mercury from flue gas and may also be applicable to

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DOI: 10.1081/SS-200030337 0149-6395 (Print); 1520-5754 (Online)

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scrubber design for removal of chlorine in the pulp and paper and other industries.

Key Words: Chlorine; Sulfite; Adsorption; Mass transfer; Reaction.

INTRODUCTION

Chlorine absorption in S(IV) (total HSO_3^- and $SO_3^=$) solutions is relevant to the simultaneous removal of Hg, Cl_2, and SO_2 from flue gas. Mercury absorption can be enhanced by reaction with chlorine oxidants.[1–6] However, the fast reaction of Cl_2 with S(IV) will deplete Cl_2 and make it unavailable for the reaction with Hg.[1]

There are several reactions that contribute to chlorine absorption in aqueous solutions. At a pH of 3 to 10.5 [with no S(IV) present], chlorine hydrolysis to form hypochlorous acid and hydrochloric acid is the dominant reaction controlling chlorine absorption.[7–9] Chlorine hydrolysis is catalyzed by buffer anions.[10,11] The following overall reaction occurs:

$$Cl_2 + H_2O + A^- \longleftrightarrow HOCl + Cl^- + HA \tag{1}$$

The kinetics of this reaction have been studied at 9.5°C for acetate, chloroacetate, and formate.[11,12] They correlated the reaction rates with the acid dissociation constant (K_a) and showed that at lower pK_a values (stronger acids), the enhancement of the hydrolysis rate was reduced.

At a pH greater than 10.5, the reaction of chlorine and hydroxide is the dominant reaction:[7,13]

$$Cl_2 + OH^- \longrightarrow Cl^- + HOCl \tag{2}$$

This reaction is relatively fast, $k_{2,OH} = 1.57 \times 10^9\,L/mol\text{-}s$;[14] thus, at high pH, there will be very little chlorine at the gas/liquid interface.

Chlorine reacts with sulfite, bisulfite, or, in the broadest sense, S(IV) to form chloride and sulfate,[15,16] but the kinetics of this reaction have not been quantified:

$$Cl_2 + H_2O + SO_3^{-2} \longrightarrow 2Cl^- + SO_4^{-2} + 2H^+ \tag{3}$$

Researchers have investigated S(IV) reactions with other chlorine oxidants including chlorine dioxide,[17] chloropeptides,[18] and chlorite.[16,19]

Fogelman et al.[20] measured the reaction kinetics of sulfite with hypochlorous acid (HOCl):

$$HOCl + SO_3^{-2} \longrightarrow OH^- + ClSO_3^- \tag{4}$$

$$ClSO_3^- + H_2O \longrightarrow Cl^- + SO_4^{-2} + 2H^+ \tag{5}$$

The first reaction has a rate constant of $7.6 \times 10^8\,L/mol\text{-}s$ at 25°C and ionic strength of 0.5, and the second reaction has a rate constant of $270\,s^{-1}$. This reaction rate is much faster than the rate of chlorine hydrolysis to form HOCl. Hypochlorite (OCl^-) also reacts with sulfite.[21,22] The reaction rate is four orders of magnitude less than the reaction rate with HOCl. A shift in mechanism is proposed to account for this difference.[20]

The objective of this work was to quantify the reaction rate of chlorine with S(IV) in the pH range where it is primarily bisulfite (HSO_3^-). Chlorine absorption in S(IV) solution was studied with various chlorine and S(IV) concentrations. The effects of oxygen, chloride, and succinate buffer were also investigated. The chlorine absorption rates were modeled using the theory of mass transfer with chemical reaction. Details on this work are presented in Roy.[1]

MASS TRANSFER WITH CHEMICAL REACTION

Chlorine absorption into S(IV) solutions occurs by mass transfer with simultaneous chemical reaction. Chlorine must diffuse from the bulk gas to the gas-liquid interface with the flux (N_{Cl_2}) given by

$$N_{Cl_2} = k_g(P_{Cl_{2,b}} - P_{Cl_{2,i}}) \tag{6}$$

Then, chlorine absorption into the liquid occurs by mass transfer with fast, irreversible chemical reaction in the boundary layer with the same flux:

$$N_{Cl_2} = \frac{Ek^o_{L,Cl_2} P_{Cl_2,i}}{H_{Cl_2}} \tag{7}$$

With the approximation developed by Glasscock,[23] the enhancement factor (E) for the irreversible reactions of chlorine with S(IV) and buffer can be expanded to give:[1,3,22,24]

$$\begin{aligned} NCl_2 &= Ek^o_{L,Cl_2} \frac{PCl_{2_i}}{HCl_2} \\ &= \frac{PCl_{2_i}}{HCl_2} \sqrt{DCl_2(k_{2,S(IV)}[S(IV)]_i + k_{2,buf}[buffer]_i)} \end{aligned} \tag{8}$$

The enhancement factor expression is derived assuming that the chlorine/S(IV) reaction is first order in chlorine and first order in S(IV). The corresponding rate expression is

$$\text{reaction rate} = k_{2,S(IV)}[Cl_2][S(IV)] \tag{9}$$

The concentrations and physical properties are known. At 25°C, the Henry's law constant for chlorine, H_{Cl_2}, was taken to be 16.7 atm-m^3/kmol,[9] and the diffusion coefficient for chlorine through water, D_{Cl_2}, was taken to be $1.48 \times 10^{-9}\,m^2/s$.[7] The chlorine flux was determined experimentally from the gas-phase material balance. The value for $k_{2,buf}$ was determined by quantifying the rate of chlorine absorption into succinate buffer. Thus, once the interfacial concentrations are calculated from the measured bulk concentrations, the only unknown is the rate constant for the chlorine/S(IV) reaction.

The interfacial liquid S(IV) concentration ($[S(IV)]_i$) is obtained by assuming that all Cl_2 reacts with S(IV) in a 1:1 stoichiometry near the gas/liquid interface.

$$N_{Cl2} = N_{S(IV)} = k^o_{L,S(IV)}([S(IV)]_b - [S(IV)]_i) \tag{10}$$

$$[S(IV)]_i = [S(IV)]_b - \frac{N_{Cl_2}}{k^o_{L,S(IV)}} \tag{11}$$

The partial pressure of chlorine at the interface can be calculated from Eq. (6), and the interfacial S(IV) concentration can be obtained from Eq. (11). The interfacial buffer concentration is assumed to be the same as the concentration of the buffer in the bulk. Thus, Eq. (8) reduces to Eq. (12):

$$N_{Cl_2} = \frac{1}{HCl_2}\left(P_{Cl_2,b} - \frac{N_{Cl_2}}{k_g}\right) \times \sqrt{DCl_2\left(k_{2,S(IV)}\left([S(IV)]_b - \frac{N_{Cl_2}}{k^o_{L,S(IV)}}\right) + k_{2,buf}[\text{buffer}]\right)} \tag{12}$$

In the stirred cell reactor, the bulk concentrations are known since the gas and liquid phases are well mixed. The partial pressure of chlorine in the bulk is equivalent to the chlorine exiting the stirred-cell reactor and can therefore be rewritten in terms of the inlet chlorine concentration through a gas-phase material balance. Thus, Eq. (13) is the resulting model used in analyzing the data from the stirred-cell reactor:

$$N_{Cl_2} = \frac{1}{HCl_2}\left(P_{Cl_2,in} - \frac{N_{Cl_2}A}{G} - \frac{N_{Cl_2}}{k_g}\right) \times \sqrt{DCl_2\left(k_{2,S(IV)}\left([S(IV)]_b - \frac{N_{Cl_2}}{k^o_{L,S(IV)}}\right) + k_{2,buf}[buffer]\right)} \tag{13}$$

For the wetted-wall column data, Eq. (12) was integrated by Euler's method to account for the changing gas and liquid concentrations. Given the chlorine and S(IV) concentrations at the bottom of the column, the model calculated the overall chlorine flux and penetration ($Cl_{2,out}/Cl_{2,in}$) in the wetted-wall column. The model values were compared with the measured flux and penetration. The rate constant was regressed by nonlinear parameter-estimation (GREG).

The rate constant can only be extracted if the chlorine absorption is controlled by kinetics. When the S(IV) concentration is high relative to the chlorine concentration, the chlorine flux is limited by the diffusion in the gas phase, and the flux from Eq. (6) simplifies to

$$N_{Cl_2} = k_g P_{Cl_{2,b}} \tag{14}$$

Under these conditions, there is essentially no chlorine at the interface since all the chlorine reacts with S(IV) as soon as the chlorine reaches the interface. Thus, the chlorine absorption only depends on how fast the chlorine diffuses from the bulk gas to the gas/liquid interface, not on the kinetics.

When the chlorine concentration is high relative to the S(IV) concentration, the flux is limited by S(IV) depletion at the interface. This means that there is essentially no S(IV) at the interface since whatever S(IV) diffuses to the interface is readily depleted through reaction with chlorine. Under these conditions, the chlorine flux at intermediate sulfite concentration is given approximately by

$$N_{Cl_2} = N_{S(IV)} = k^o_{L,S(IV)}[S(IV)]_b \tag{15}$$

showing that the flux of chlorine is linear with the bulk S(IV) concentration. At low or zero sulfite the flux will also include a contribution from the chlorine reaction with the buffer.

EXPERIMENTAL APPARATUS AND METHODS

All chlorine absorption experiments were performed at ambient temperature (22 to 25°C) and atmospheric pressure. Teflon tubing, fittings, and valves were used for all the connections.

Description of Stirred Cell Reactor

Initial experiments were conducted in a well-characterized stirred cell contactor with Teflon surfaces.[1,3,25] Both gas and liquid phases were agitated and the reactor was baffled, giving an unbroken, reasonably smooth liquid surface. The total volume of the reactor was $1.295 \times 10^{-3}\,\mathrm{m}^3$, while the volume of solution in a typical experiment was $1.06 \times 10^{-3}\,\mathrm{m}^3$. The stirred-cell contactor allowed gas-liquid contact, for which mass-transfer properties were known or measured, at a known interfacial area (A) of $8.1 \times 10^{-3}\,\mathrm{m}^2$. A detailed description of the reactor is provided in Roy.[1]

Gas Source and Flow Path for Stirred Cell Reactor

Gas feed was prepared by quantitatively mixing 0.1% Cl_2 (1000 ppm in N_2) with pure nitrogen. For the experiments containing oxygen, the chlorine was diluted with house air (instead of pure N_2) before entering the reactor. The synthesized gas stream, typically at a flow rate of 1.2 L/min, was continuously fed to the reactor. After exiting the reactor, the gas stream was diluted with house air and a portion of the gas was continuously analyzed for chlorine.

Chlorine Analysis

The chlorine analyzer (Molecular Analytics AirSentry 10-Cl2) operated on the principle of ion mobility spectrometry (IMS), which is similar to time-of-flight mass spectrometry.[26] During calibration, the gas flow rate was identical to that in an experiment. Other than bypassing the reactor, the gas flow path during calibration was the same as during an experimental run. The analyzer was calibrated with nitrogen and Cl_2/N_2 mixtures spanning the range of interest.

Stirred Cell Reactor Solution and Analysis

The reactor contained the aqueous S(IV) solution, ranging from 0 to 10 mM, used in absorbing chlorine. The reactor solution was buffered by injecting a stock solution of succinic acid/sodium hydroxide. The S(IV) solution was obtained by injecting a stock solution containing equimolar sodium bisulfite and sodium sulfite.

Liquid samples were taken from the bulk of the reactor and analyzed for S(IV) concentration by iodometric titration.[1,27] Due to uncertainties in initial experimental methods at low S(IV),[1] the expected precision at S(IV) concentrations below 0.09 mM is ± 0.04 mM. However, the S(IV) concentrations were more precise in the wetted-wall column experiments due to modifications such as withdrawing larger samples and using lower-concentration standards.

Description of Wetted-Wall Column

Chlorine absorption experiments were also conducted in the wetted-wall column depicted in Fig. 1.[1] The column consists of a glass tube divided into five 6-cm sections. The liquid solution is collected and refreshed between sections. The column has a 1-cm ID, 108 cm^2 area, and a total height of 31 cm. Gas flows into the bottom of the column through a 3/8-in. OD glass tube and counter-currently contacts the liquid. This glass tube has a smooth, sharp edge (ground outward as shown in Fig. 1) in order to ensure that no liquid enters it. All surfaces in contact with gas are either glass or Teflon to avoid adsorption.

Aqueous solution enters the top glass reservoir (which is maintained full of liquid throughout an experiment), and the liquid enters the column and distributes itself evenly. To aid in an even liquid distribution, the inside face of the tube (in each of the five sections) was ground downward. Liquid is collected in the bottom glass reservoir and pumped using a gear pump. The top reservoir holds approximately 25 mL of liquid, while the bottom reservoir holds about 30–40 mL.

Wetted-Wall Column Solution Flow Path and Analysis

Figure 2 shows a flow diagram of the complete wetted-wall apparatus with all the supporting equipment. The liquid solution was stored in a reservoir of 0.7 L or 3.1 L. The liquid flow rate was measured using a rotameter. The range of operating liquid flow rates was very narrow (2 to 3.5 mL/s) due to the flow stability and entrainment. The typical flow rate was 2.26 mL/s.

A two-head Masterflex peristaltic pump was used to withdraw samples of the solution exiting the column, while adding fluid to the reservoir to retain the liquid level. Liquid samples were periodically taken from the liquid outlet and analyzed using iodometric titration. Samples of 20 to 50 cm^3 were pumped directly into an Erlenmeyer flask with iodine solution.

During a typical experiment, the absorption of chlorine into the buffer was first measured. After this measurement, the experiments consisted of 1) injecting S(IV) into the reactor; 2) withdrawing samples for analysis as the S(IV) was depleted; and 3) injecting more S(IV) and analyzing samples.

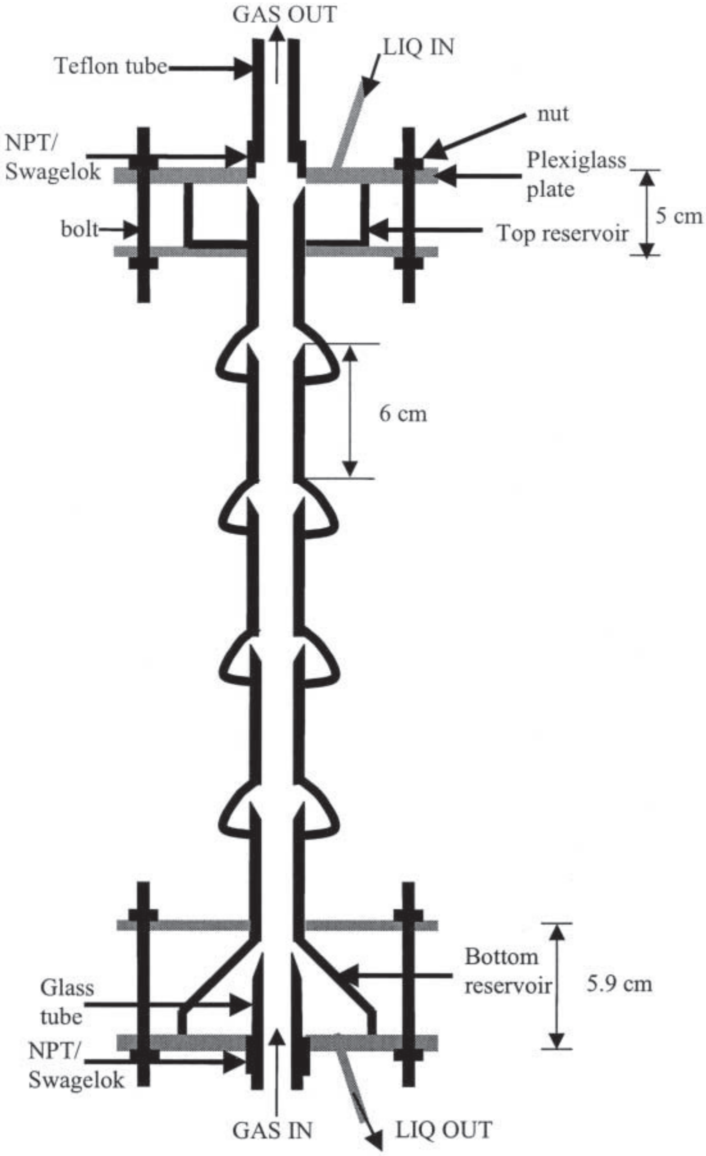

Figure 1. Wetted wall column.

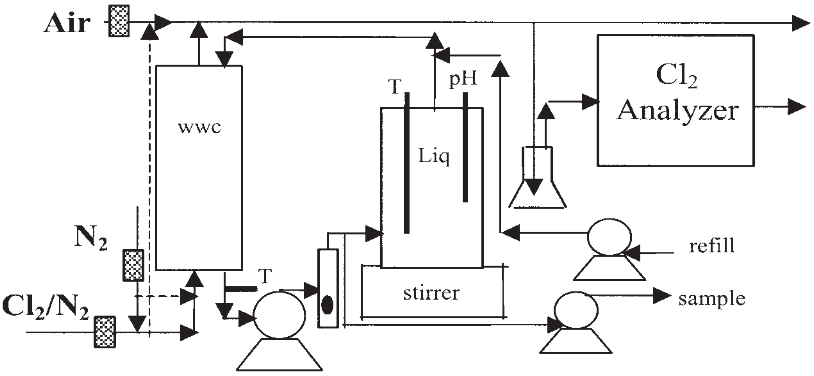

Figure 2. Flow diagram for chlorine absorption in wetted wall column.

Throughout a single experimental series, the chlorine inlet concentration was usually kept constant.

For the experiments at pH 5.7, the procedure was slightly different. The experiment started with absorption in buffer, while varying the chlorine inlet. Then, S(IV) was added, and the chlorine inlet was again varied at several S(IV) concentrations. The S(IV) was periodically sampled, but it was not measured at every data point.

Gas Flow Path in Wetted-Wall Column

As with the stirred cell experiments, gas flow rates were controlled by mass flow controllers. The synthesized gas stream, typically ranging from 5 to 10 L/min, was continuously fed to the column. The dashed lines in Fig. 3 represent alternate flow paths. The chlorine and nitrogen can both bypass the column, or the chlorine alone can bypass the column. The column could not operate at gas flow rates greater than 10 L/min because liquid would be forced out through the gas exit. After exiting the column, the gas was diluted with air. Most of the gas was vented to the hood, while a portion of it passed through a knockout flask before entering the Cl$_2$ analyzer.

Mass Transfer Coefficients

The gas-phase mass-transfer coefficient was determined by measuring chlorine absorption in 0.25 M sodium hydroxide, and the liquid-phase coefficient was determined by measuring chlorine desorption from sodium hypochlorite solution in 0.1 M hydrochloric acid.[1]

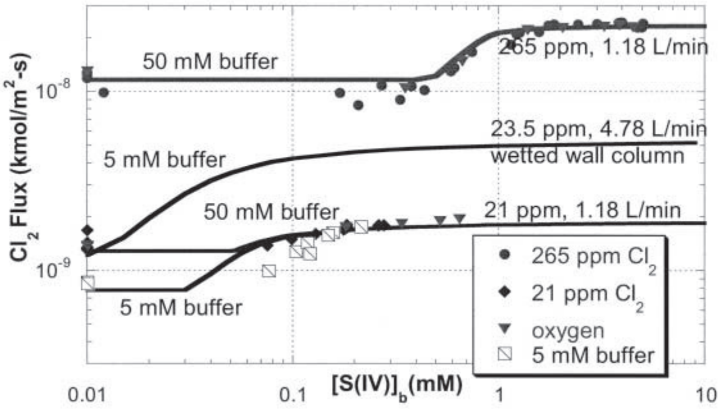

Figure 3. Chlorine absorption in buffered S(IV) at pH 4.7 with data from stirred cell reactor, Curves calculated with $k_{2,S(IV)} = 1 \times 10^9$ L/mol-s.

The mass-transfer coefficients for the stirred cell reactor were a function of the agitation rates as shown in Eqs. (16) and (17). Typical agitation rates ranged from 700 to 750 rpm.

$$k_g(\text{mol/s-atm-m}^2) = 0.0252(n_g)^{0.5142} \tag{16}$$

$$k^o_{L,Cl_2}(\text{m/s}) = 6.591 \times 10^{-7}(n_L)^{0.56} \tag{17}$$

The mass-transfer coefficients for the wetted-wall column were a function of the flow rates. At a typical gas-flow rate of 4.78 or 9.52 L/min, the k_g was 0.4 or 0.7 mol/s-atm-m^2, respectively.[1] At a typical liquid flow rate of 2.26 mL/s, the liquid film mass-transfer coefficient was 9×10^{-5} m/s.[1]

The gas/liquid contact area for the wetted-wall column was determined from measuring the absorption of CO_2 in NaOH.[1] The area was determined to be 108 cm^2, which was slightly higher than the geometric area. The contact area of the stirred cell reactor was assumed to be its geometric area of 81 cm^2. It was baffled and appeared to have a flat liquid surface.

RESULTS AND DISCUSSION

Rate of Reaction for Chlorine with S(IV)

Figure 3 depicts the chlorine flux, measured using the stirred cell reactor, as a function of the bulk S(IV) concentration at pH 4.7. Data at two chlorine inlet concentrations of 265 ppm and 21 ppm are shown. The points at 0.01 mM S(IV) are actually in succinate buffer with no S(IV). The inverted triangles in Fig. 3 represent points in which 15 to 20% oxygen was added. All the data are in 50 mM succinate buffer (50 mM succinic acid-50 mM NaOH) except for the points represented by the squares with diagonal lines which are in 5 mM buffer (5 mM succinic acid-5 mM NaOH). The data are tabulated in Roy.[1]

At low pH and high S(IV), $SO_2(g)$ production occurs. Therefore, data in experiments with greater than 5 mM S(IV) for the 265 ppm inlet and greater than 1 mM S(IV) for the 21 ppm inlet were discarded because SO_2 was stripped from the reactor and reacted with Cl_2 on the damp surfaces of downstream equipment.

The curves for the stirred cell reactor are calculated using Eq. (13.) The gas flow rate (1.18 L/min) and mass-transfer coefficients used in the model were representative of the experimental data. The gas and liquid phase mass-transfer coefficients (k_g and $k^o_{L,S(IV)}$) in the model for the stirred cell reactor were $0.75\,\mathrm{mol/s\text{-}atm\text{-}m^2}$ and $2.45 \times 10^{-5}\,\mathrm{m/s}$, respectively. The rate constant of the chlorine/S(IV) reaction ($k_{2,S(IV)}$) was chosen to best fit the data. The buffer rate constant was obtained from analysis of the chlorine absorption in succinate buffer experiments which will be discussed later in this paper. Figure 3 also shows the predicted curve for the wetted-wall column.

Figure 3 shows that at high S(IV), the chlorine flux does not depend on the S(IV) concentration since the limit of gas-film resistance is approached. At lower chlorine concentrations, gas-film control is achieved at lower S(IV) since it takes less S(IV) to react with the chlorine. The data from Fig. 3 also show that at low S(IV), the flux is limited (in some cases inhibited) by the buffer-enhanced chlorine hydrolysis reaction. In this region, the flux depends mainly on the buffer reaction rate.

Since Fogelman et al.[20] have shown that HOCl reacts with sulfite, one possible mechanism for chlorine reaction with S(IV) is that the chlorine first hydrolyzes in water to form HOCl, and then the HOCl (not Cl_2 directly) reacts with S(IV). These overall reactions are shown below:

$$Cl_2 + H_2O \longrightarrow HOCl + H^+ + Cl^- \tag{18}$$

$$HOCl + SO_3^{-2}/HSO_3^- \longrightarrow SO_4^{-2} + H^+/2H^+ + Cl^- \tag{19}$$

If this were the case, the rate of chlorine absorption in S(IV) would be equivalent to the rate of chlorine hydrolysis to form HOCl since chlorine hydrolysis is the rate limiting step. Then, the HOCl would react with S(IV). However, since the addition of S(IV) results in a greater chlorine removal rate than the chlorine hydrolysis rate, it must not depend on HOCl formation.

Thus, chlorine itself reacts with S(IV) directly, and it is not necessary for HOCl to form before chlorine reaction with S(IV) occurs.

For the data at intermediate S(IV) concentrations in Fig. 3, the flux is limited by S(IV) diffusion to the interface [depicted by flux increasing linearly with S(IV)] and/or kinetics (depicted by curvature). In the stirred cell reactor, there is only a very small range (depicted by curvature) where the chlorine flux should be limited by the kinetics of the Cl_2/S(IV) reaction. Thus, it is hard to extract a precise rate constant, with a reasonable confidence interval, from the stirred cell reactor since most of the data falls in a region where the chlorine absorption is not limited by kinetics.

Therefore, chlorine absorption experiments were also conducted in a wetted-wall column, which had a higher liquid-film mass-transfer coefficient. The wetted-wall column model in Fig. 3 shows that the range between the buffer-enhanced chlorine hydrolysis rate and gas-film control is greater than it was in the stirred-cell reactor. The curvature is also broader, which signifies a region where the absorption is limited by kinetics.

Experiments were conducted at pH 4.7 and 5.7 in the wetted-wall column. All data are tabulated in Roy.[1] Table 1 gives the experimental conditions and model parameters used with these experiments, including the regressed-rate constants. Figures 4 and 5 compare the measured Cl_2 penetration to that calculated by Eq. (12.) Since the concentrations change throughout the column, the model was integrated to obtain the bulk concentrations at each point in the column. The S(IV) concentrations in Fig. 4 and 5 are represented as the outlet concentration (normalized by the chlorine inlet) because the liquid was sampled at the outlet.

Figures 4 and 5 depict the same general trends as the stirred cell data. At high S(IV), the chlorine penetration flattens since the limit of gas-film resistance is approached. Figure 4 also shows the effect on the penetration when the $k_{2,S(IV)}$ is varied by an order of magnitude. The model is very sensitive to the Cl_2/S(IV) reaction rate. Thus, the wetted-wall column

Table 1. Values of parameters used to model chlorine absorption at 25°C.

Parameter	pH 4.7	pH 5.7
[succinic acid]$_T$ (mM)	5.0	2.78
[NaOH] (mM)	5.0	5.0
$k_{2,buf}$ (L/mol-s)	1.5×10^5	8.5×10^5
G (L/min)	4.78 or 9.52	4.78
k_g (mol/s-atm-m^2)	0.4 or 0.7	0.4
$k^o_{L,S(IV)}$ (m/s)	8.53×10^{-5}	8.53×10^{-5}
$k_{2,S(IV)}$ (L/mol-s)	1.0×10^9	1.4×10^9

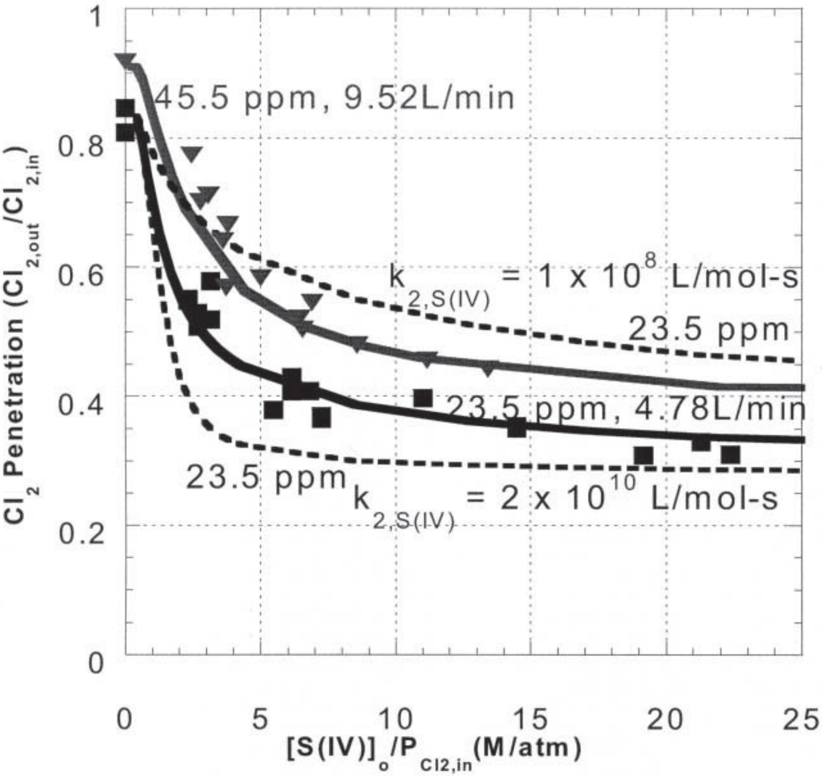

Figure 4. Chlorine penetration in buffered S(IV) at pH 4.7 in wetted wall column, Solid curves calculated using $k_{2,S(IV)} = 1.0 \times 10^9$ L/mol-s, Dashed curves calculated by varying $k_{2,S(IV)}$ at 23.5 ppm Cl_2 and 4.78 L/min.

resulted in the extraction of a more precise rate constant than the stirred-cell reactor.

At pH 4.7, a rate constant with a 95% confidence interval of $(1.0 \pm 0.2) \times 10^9$ L/mol-s was regressed from the data. This rate constant fits the wetted-wall column data very well and also fits the stirred-cell reactor data (as shown by Fig. 3). At pH 5.7, the regressed-rate constant was $(1.4 \pm 0.5) \times 10^9$ L/mol-s, which is slightly greater than the value at pH 4.7. However, the uncertainty is greater also. The lack of precision at pH 5.7 probably results from the difference in procedure and the narrower range in observable flux/penetration. Since these rate constants are very similar, an average value of $(1.1 \pm 0.3) \times 10^9$ L/mol-s can be reported for the Cl_2/S(IV) rate constant.

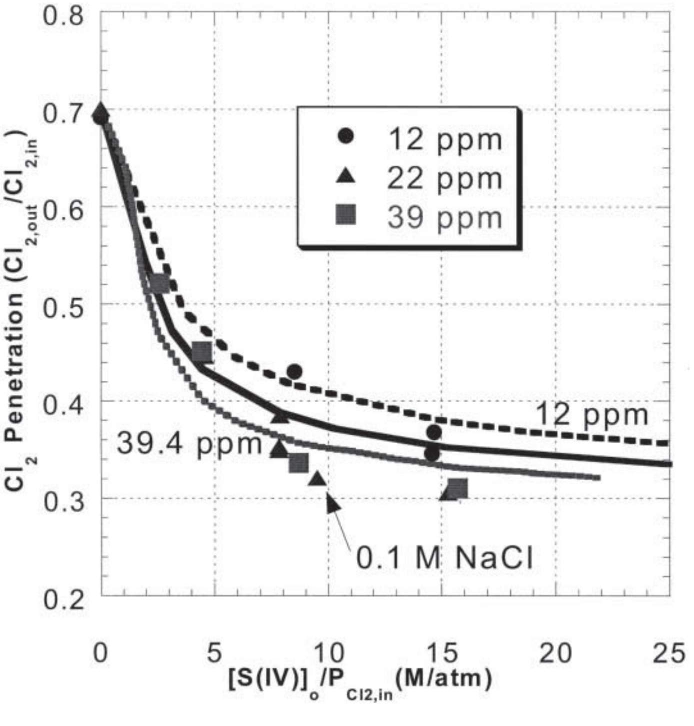

Figure 5. Chlorine penetration in buffered S(IV) at pH 5.7 in wetted wall column, Curves calculated using $k_{2,S(IV)} = 1.4 \times 10^9$ L/mol-s.

Effect of 0.1 M NaCl

A data point with 0.1 M sodium chloride at pH 5.7 is plotted in Fig. 5. The chloride did not have a statistically significant effect on the $Cl_2/S(IV)$ reaction rate. Since the $Cl_2/S(IV)$ reaction is irreversible, the addition of chloride should not affect the absorption rate, unless the solution is at a very high ionic strength where activity coefficient corrections may become significant.

Comparison of S(IV) Reaction Rates with $Cl_2/HOCl/OCl^-$

Fogelman et al.[20] quantified the reaction rates of S(IV) with hypochlorous acid (HOCl) and hypochlorite (OCl^-). The reaction rate decreased with pH, as the HOCl was converted to OCl^-. Table 2 tabulates the rate constants

Table 2. Reaction rates of S(IV) with chlorine species at 25°C.

Chlorine species	Rate constant for reaction with S(IV) (L/mol-s)
Cl_2	1.1×10^9
HOCl	7.6×10^8
OCl^-	2.3×10^4

for the reaction of S(IV) with Cl_2 (obtained from this work), HOCl, and OCl^-. All reaction rates were first order in S(IV) and first order in the chlorine species.

At high pH, OCl^- is the dominant species. As the pH is decreased, HOCl becomes the dominant species, and the reaction rate with S(IV) is four orders of magnitude faster.[20] As the pH is decreased further, chlorine is the dominant species, resulting in an even faster reaction rate with S(IV).

Enhancement of the Chlorine Hydrolysis Rate by Succinate

Chlorine absorption was measured as a function of succinate concentration without S(IV). Figure 6 gives the results at pH 4.7 in the stirred-cell

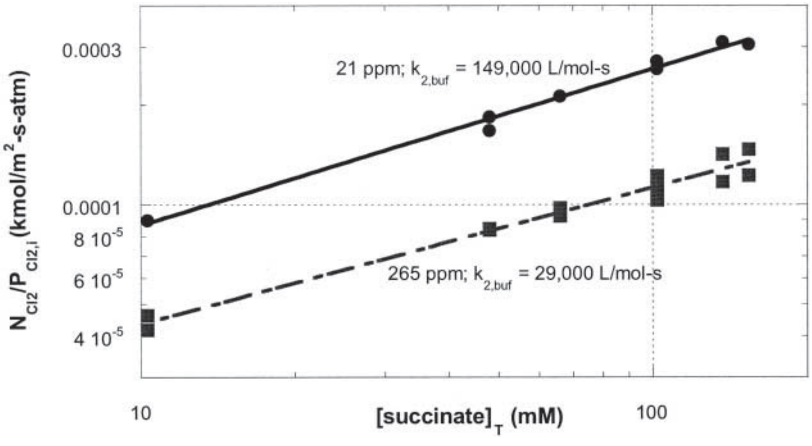

Figure 6. Obtaining kinetics for chlorine absorption in succinate buffer at pH 4.7 in stirred cell reactor.

reactor. All data are tabulated in Roy.[1] The absorption rate was modeled by Eq. (13) with the kinetics given by Eq. (20):

$$\text{rate} = k_{2,\text{buf}}[\text{Cl}_2][\text{A}^-] \tag{20}$$

where $[\text{A}^-]$ is the concentration of anion equivalents, which is equal to the Na^+ concentration in the buffer.

The rate constant, $k_{2,\text{buf}}$, extracted from the data shows a dependence on the gaseous chlorine concentration, with values of 2.9×10^4 L/mol-s at a Cl_2 inlet of 265 ppm and 1.49×10^5 L/mol-s at 21 ppm Cl_2.

Figure 5 gives absorption data at pH 5.7 without S(IV) in the wetted-wall column. The regressed value for $k_{2,\text{buf}}$ for these data is $(8.5 \pm 0.5) \times 10^5$ L/mol-s. This rate is higher than the rate for enhancement in the pH 4.7 buffer.

Lifshitz and Perlmutter-Hayman[8] found that the rate constants (k_A) at 9.5°C were correlated by

$$k_A = 1.6(K_a)^{-0.54} \tag{21}$$

At pH 4.7, the succinate buffer has an effective pK_a of 4.21.[28] At pH 5.7, the effective buffer is di-succinate, with a pK_a of 5.64.[28] Therefore, our measured reaction rates with 22 ppm Cl_2 suggest that the rate constants in succinate buffer at 25°C are given by Eq. (22):

$$k_A = 770(K_a)^{-0.54} \tag{22}$$

Our data have the same dependence on K_a as observed by Lifshitz and Perlmutter-Hayman.[11] However, the absolute rate is greater, perhaps resulting from the higher temperature or the unexplained dependence on the Cl_2 partial pressure.

S(IV) Oxidation by Chlorine and Oxygen

Chlorine and oxygen both oxidize S(IV) to sulfate, S(VI). Since other oxidants, such as NO_2, are known to enhance oxygen absorption,[29] experiments were conducted in the stirred-cell reactor to see if chlorine enhanced oxygen absorption. These experiments established that Cl_2 is not a catalyst for the oxidation of S(IV) by O_2. Table 3 shows how the oxidation of S(IV) depends on oxygen and chlorine. The observed S(IV) oxidation rate was calculated from the depletion rate of S(IV) over time. All data are tabulated in Roy.[1]

Table 3 shows that the effects of Cl_2 and O_2 on S(IV) oxidation may be additive when the inlet concentration is 275 ppm Cl_2. The expected oxidation

Table 3. S(IV) oxidation by chlorine and oxygen in 50 mM succinate buffer at pH 4.7.

Cl_2 inlet (ppm)	O_2 inlet (%)	S(IV) oxidation rate (mol/m^2-hr)	[S(IV)] range (mM)
0	14.5	0.037	1 to 5
275	0	0.095	1 to 5
275	14.5	0.13	1 to 5
0	20.5	0.068	1 to 5
21	0	0.004	1 to 4
21	20.5	0.017	0.2 to 0.5
		0.059	0.6 to 2
		0.099	3 to 5

rate of S(IV) resulting from the physical absorption of 14.5% O_2 was calculated to be 0.039 mol/m^2-h. This value agreed with the observed value of 0.037 mol/m^2-h. When only chlorine is absorbed, the oxidation of S(IV) is 0.095 mol/m^2-h. The ratio of the rate of S(IV) oxidation to the rate of Cl_2 absorption was 1:1, confirming the 1:1 stoichiometry of the Cl_2/S(IV) reaction. When chlorine and oxygen are simultaneously absorbed [corresponding to S(IV) oxidation rate of 0.13 mol/m^2-h], about three-fourths of the S(IV) oxidation is due to the reaction of chlorine with S(IV). In this case, the chlorine does not seem to be catalyzing S(IV) oxidation since the S(IV) oxidation seems to be additive.

The oxidation rates using 22 ppm Cl_2 show that the oxidation of S(IV) due to reaction with chlorine alone is practically negligible since the chlorine concentration is significantly lower. At this Cl_2 concentration, when Cl_2 and O_2 were simultaneously absorbed, the rate of S(IV) oxidation depended on the level of S(IV). Physical absorption of 20.5% oxygen corresponds to S(IV) oxidation of 0.055 mol/m^2-h. Thus, the oxidation rate of S(IV) without chlorine obtained experimentally is in the range of the calculated oxidation rate due to physical absorption of O_2. At very low S(IV) concentrations ($<$0.5 mM), the S(IV) oxidation is much less (0.017 mol/m^2-h) than that expected from physical absorption of oxygen. This may occur because at these low concentrations, there is barely any S(IV) at the interface. When S(IV) is between 0.5 and 2 mM, it seems that the S(IV) oxidation is equivalent to that which would result from the physical absorption of oxygen. Thus, chlorine does not seem to enhance S(IV) oxidation in this case. At high S(IV) concentrations (around 4 mM), the S(IV) oxidation is much greater at 0.099 mol/m^2-h. Chlorine may be catalyzing S(IV) oxidation. This may also reflect stripping of SO_2 from the solution. More data would need to be taken in this range.

CONCLUSIONS

The addition of S(IV) significantly enhances chlorine absorption. The rate constant was too rapid to be precisely measured using the stirred-cell reactor, due to mass-transfer limitations. However, the range of kinetics-limited absorption was greater using the wetted-wall column. Using the wetted-wall column, the $Cl_2/S(IV)$ reaction rate constant with a 95% confidence interval was determined to be $(1.1 \pm 0.3) \times 10^9$ L/mol-s. The addition of up to 0.1 M sodium chloride did not affect the rate of Cl_2 absorption in S(IV).

The S(IV) reacts with chlorine directly, not through the formation of HOCl. The reaction rate of S(IV) with chlorine is greater than that with HOCl and OCl^-. The reaction is very rapid, requiring only 0.2 mM S(IV) to become gas-film-controlled with 20 ppm Cl_2. The S(IV) required to reach gas-film control depends on the chlorine concentration. When the partial pressure of the inlet chlorine (in atm) is 10 times less than the S(IV) concentration (in mol/L), the absorption becomes gas-film controlled.

At low S(IV) concentrations, the chlorine absorption was limited by the buffer-enhanced hydrolysis reaction. The enhancement by the succinate buffer was quantified. The di-succinate results in greater enhancement of Cl_2 absorption than the mono-succinate anion.

Oxygen did not affect the rate of chlorine absorption in S(IV); also, it did not catalyze S(IV) oxidation at the conditions investigated. With no oxygen present, the rate of S(IV) oxidation was equal to the rate of chlorine absorption, confirming the reaction stoichiometry of 1 mole Cl_2 per 1 mole S(IV).

NOMENCLATURE

A	Gas/liquid contact area (m^2)
A^-	Generic anion
D_{Cl_2}	Diffusion coefficient for chlorine in water (m^2/s)
E	Enhancement factor (dimensionless)
FC	Mass flow controller
G	Gas flow rate to reactor (m^3/s or L/min)
HA	Generic acid
H_{Cl_2}	Henry's law constant for chlorine (atm-m^3/kmol)
IMS	Ion mobility spectrometry
k_g	Individual gas-film mass-transfer coefficient (kmol/s-atm-m^2)
k^o_{L,Cl_2}	Individual physical liquid-film mass-transfer coefficient for chlorine (m/s)
$k_{1,H2O}$	First-order rate constant for chlorine hydrolysis reaction (s^{-1})

$k_{2,buf}$	Second-order rate constant for chlorine/succinate buffer reaction (m^3/kmol-s)
$k_{2,S(IV)}$	Second-order rate constant for chlorine/S(IV) reaction (m^3/kmol-s)
$k_{2,OH}$	Second-order rate constant for chlorine/hydroxide reaction (m^3/kmol-s)
N_{Cl_2}	Flux of chlorine (kmol/m^2-s)
n_g	Gas phase agitation rate (rpm)
n_L	Liquid phase agitation rate (rpm)
P	Total pressure (atm)
P_{Cl_2}	Partial pressure of chlorine (atm)
$P^*_{Cl_2,b}$	Partial pressure of chlorine in equilibrium with chlorine in bulk liquid (atm)
pK_a	Negative logarithm of acid dissociation constant

Subscripts

b	In bulk
Cl_2	For chlorine
i	At gas/liquid interface
in	Inlet
L	Liquid
o	Outlet
S(IV)	For S(IV)
T	Total

ACKNOWLEDGMENTS

Sharmistha Roy was supported by a fellowship from the Texas Utilities Environmental Research Steering Committee. Other support was provided by EPA CR 827608-01-1.

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Received July 11, 2003
Accepted July 6, 2004