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Chlorine Absorption Utilizing Caustic Sodium Sulfite

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CHLORINE ABSORPTION UTILIZING
CAUSTIC SODIUM SULFITE

A Thesis
Presented to
the Graduate School of
Clemson University

In Partial Fulfillment
of the Requirements for the Degree
Master of Science
Chemical Engineering

by
Henry Evan McDonald
December 2011

Accepted by:
Dr. Charles Gooding, Committee Chair
Dr. Scott Husson
Dr. David Bruce

ABSTRACT

A scrubber was required to abate a waste stream containing chlorine gas created in the electrolytic dissolution step of the aqueous polishing process at the Mixed Oxides Fuel Fabrication Facility at Savannah River Site, South Carolina. A method of absorption that utilized caustic sodium sulfite as the scrubbing agent was studied for implementation in the process. This method was found to be highly efficient with respect to process requirements, and it was also found to provide enhanced performance over the more conventional method of chlorine scrubbing which uses only aqueous sodium hydroxide as a reagent. Sulfite provides an additional advantage in that it scavenges other potential pollutants such as hypochlorite and prevents their desorption back into the gas stream. Absorption was found to be rate-limited by liquid phase mass transfer at low to medium sulfite concentrations. The process is believed to be rate-limited by gas phase mass transfer at higher sulfite concentrations, although specific conditions for gas phase control could not be determined. A significant amount of the sulfite was found to be consumed by an undesirable oxidation side reaction. The process was found to be mildly exothermic, but heat effects were not detrimental to system performance.

DEDICATION

The author would like to dedicate this work to his parents, Dr. and Mrs. Timothy and Deborah McDonald.

ACKNOWLEDGMENTS

Thanks to the U.S. Department of Energy for funding this research. The author would like to express his sincere gratitude to his advisor, Dr. Charles Gooding, for his guidance, support, and hard work on this project. Very special thanks also to the other members of the committee, Dr. Scott Husson and Dr. David Bruce, for their help and their many excellent suggestions for improvements. This work was carried out at the Clemson Engineering Technologies Laboratory. Thanks go out to all the staff there, but particularly to John Harden and Steve Hoeffner. Without their guidance the author would have been hopelessly lost, and it was a true pleasure to work with them. Thanks also to Jamie Kearns, Michael McCulley, and Will Vining, who contributed much helpful insight during the early stages of this project. Lastly the author would like to thank his family for their love, support, and ever-amusing companionship.

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ORIGIN AND SCOPE

The Mixed Oxide (MOX) Fuel Fabrication Facility is a process being constructed at Savannah River Site of the Department of Energy (DOE). The purpose of the facility is to process decomposed weapons grade plutonium into fuel grade plutonium. The aqueous polishing process includes a dechlorination and dissolution process referred to as the KDD. In the KDD unit, PuO_2 is dissolved into a nitric acid solution by application of a direct current. Insoluble chlorides and other impurities present in the PuO_2 are transformed into gases during the electrolytic dissolution of PuO_2 . A waste stream is created consisting mainly of air and chlorine. Other impurities such as HNO_2 , HNO_3 , NO , NO_2 , N_2O_4 , H_2 , H_2O , N_2 , and O_2 are present as well, but only in trace amounts. A scrubber is needed to abate 99.5 % to 99.995 % of these pollutants. To simplify the experimental work, only Cl_2 will be considered for the purposes of this study.

Objectives

The purpose of this work was to design, build, and test a chlorine scrubber to operate at the conditions to be used in the MOX Fuel Fabrication Facility. Special attention was paid to aspects of design and operation that allow for safe and effective running of the equipment.

Some of the basic operating conditions specified by DOE for test purposes were:

- Gas flow rate should be constant at approximately 25 L/min at STP
- The maximum load of Cl_2 gas to be processed is approximately 0.72 kg/hr.
- The pH of the scrubbing liquor should remain constant at 12 in order to allow for high scrubbing capacity and to limit corrosion.

- The scrubbing solution must utilize Na_2SO_3 as the scrubbing agent and NaOH to maintain the desired pH.
- The packing should be 750 Mellapak-Y by Sulzer.

Experiments were intended to yield insight on the effects of the following variables on scrubber performance:

1. Sulfite concentration
2. Inlet Cl_2 concentration
3. Inlet air flowrate
4. Recirculation rate
5. Packing height
6. Capacity of the scrubbing liquor for absorption of chlorine

Beyond designing a process that was capable of accomplishing the main practical objectives, an additional goal of this project was to understand as well as possible the fundamental molecular processes taking place. Of specific interest was the understanding of the absorption process within the context of mass transfer and chemistry.

LITERATURE REVIEW

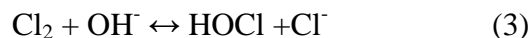
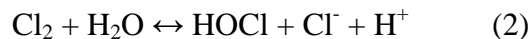
A fundamental understanding of this chlorine scrubbing process requires insight into the mass transfer, chemical reaction kinetics, and thermodynamics of the system. Determination of which of these factors limits the rate of chlorine absorption is crucial to understanding the key design parameters. Transport of Cl₂ gas into aqueous solution occurs by mass transfer with simultaneous chemical reaction in the liquid phase. The first task is to catalogue and characterize the chemical reactions taking place in the system.

Reactions involving Chlorine and Aqueous Sodium Hydroxide

Chlorine reacts in alkaline sulfite solutions in numerous ways, creating a complex network of reactions. The first task is to understand how Cl₂ behaves in a simple aqueous solution at different pH values. Water dissociates into hydroxide and hydronium ions; this reaction can be represented by Eq. (1).



As Cl₂ is dissolved into aqueous solution, it undergoes hydrolysis by two reactions, as represented in Eq. (2) and (3).



Which reaction is favored is dependent on pH. Spalding (1962) showed that above pH 12.6 reaction (3) is favored and rate controlling, while below pH 10.5 reaction (2) is favored. Kinetic data for Cl₂ hydrolysis involving the forward and reverse reactions of Eq. 2 are presented in table 2.1 (Wang and Margerum, 1994).

Table 2.1: Rate Data for Cl₂ Hydrolysis

T (°C)	k ₂ (s ⁻¹)	k ₂ × 10 ⁻³ M ⁻² s ⁻¹
0	1.9 +/- 0.1	7.1 +/- 0.3
5	1.9 +/- 0.1	9.7 +/- 0.5
10	5.7 +/- 0.2	12.0 +/- .4
15	9.1 +/- 0.3	15.2 +/- 0.6
20	15.0 +/- 0.4	18.2 +/- 0.7
25	22.3 +/- 0.6	21.4 +/- 0.8
30	30.5 +/- 0.9	26.2 +/- 0.9

The equilibrium constant data for Cl₂ hydrolysis (Eq. 2) have been studied by a number of sources. The work of Connick and Chia (1958) is tabulated in table 2.2. The data in this table are given as apparent equilibrium constants which assume ideal solution and include the reference fugacities of the true equilibrium constant.

$$K_2 = \frac{k_2}{k_{-2}} = \frac{[H^+][Cl^-][HOCl]}{[Cl_2]} \quad (4)$$

Table 2.2: Apparent Equilibrium Constant data for Cl₂ hydrolysis at different temperatures

T (°C)	K ₂ × 10 ⁴ (M ²)
0	1.46
15	2.81
25	3.94
35	5.1
45	6.05

Gershenson (2002) reports a rate of reaction for Eq. 3. He also shows that reaction rates for Eq. 2 and 3 are equal at pH (6.6). He reports that reaction 3 is dominant above pH 6.6, which is a lower value than that reported by Spalding (1962). The kinetic data compiled by Gershenson are displayed in table 2.3. No data are available for the reverse reaction.

Table 2.3: Rate constants for forward reaction of Cl₂ with hydroxide (Gershenzon, 2002)

T (°C)	k ₃ × 10 ⁻⁸ M ⁻¹ s ⁻¹
2	1.3 +/- 0.5
20	6 +/- 2
30	8 +/- 3

The dimensionless true equilibrium constant for reaction 3 is given by Hikita et al. (1973) at 30°C in Eq. 5:

$$K_3 = \frac{[HOCl][Cl^-]}{[Cl_2][OH^-]} = 3.1 \times 10^{10} \quad (5)$$

The high value of the equilibrium constant means that the amount of Cl₂ reacted and thus the amount of HOCl present depends strongly on the pH of the solution in the basic range. Whether reaction (2) or (3) is the rate controlling one in a given system is dependent upon pH. Spalding (1962) studied the kinetics of Cl₂ hydrolysis at different values of pH. Rate of Cl₂ absorption is shown as the enhancement factor, Φ, which is defined as the rate of absorption with chemical reaction divided by the rate of absorption with no chemical reaction. Figure 2.1 shows the behavior of Φ over a wide range of pH.

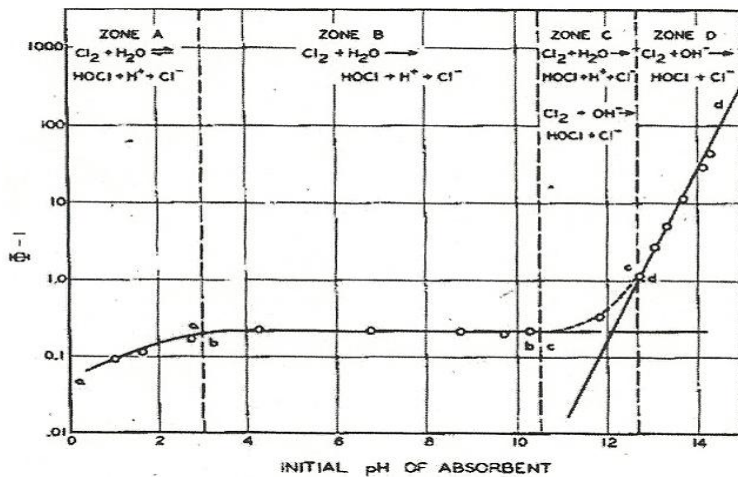


Figure 2.1: Enhancement factor minus one as a function of pH, Spalding (1962). Reprinted with permission from Wiley and Sons

As can be seen from Figure 2.1, Eq. 2 is the dominant reaction below pH 2, with the absorption rate increasing as pH increases. This trend is observed because at low pH there is a high concentration of H⁺ ions, which causes the reverse reaction to be more significant. Above pH 3, the concentration of H⁺ ions becomes insignificant and the forward reaction is dominant. Between pH 3 and pH 10.5, Eq. 2 is still the rate controlling reaction, but the rate of absorption is approximately constant over this range as the reverse reaction is insignificant. Between pH 10.5 and pH 12.5, a transition region is observed where Φ begins to increase nonlinearly. This takes place due to the combined effects of the forward reaction of Eq. (2) and Eq. (3), which is now significant due to the increasing pH, and thus increasing concentration of OH⁻ ions. As pH passes 12.5 the concentration of OH⁻ ions is now high enough to cause Eq. (3) to be rate controlling. Consequently, Φ increases linearly with pH (Spalding, 1962).

After hypochlorous acid is produced via Eq. (2) or Eq. (3), it can then react with hydroxide to form hypochlorite according to Eq. (6) or Eq. (7). Hikita et al. (1973) believed this reaction also affects absorption rate.

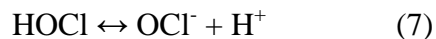
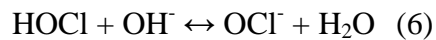


Table 2.4 presents kinetic data for the forward (k_6) and reverse (k_{-6}) reactions of Eq. 6 at 25°C.

Table 2.4: Rate constants for dissociation of hypochloric acid at 25°C
(Fogelman et al., 1989)

k_6	$3.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$
k_{-6}	$1.8 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$

The value of the apparent equilibrium constant of reaction 6 at 30°C is shown in equation 8 (Hikita et al., 1973). This value is consistent with the data from Fogelman et al. (1989) in Table 2.4.

$$K_6 = \frac{[OCl^-]}{[HOCl][OH^-]} = \frac{k_6}{k_{-6}} = 2.2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1} \quad (8)$$

$$K_7 = \frac{[H^+][OCl^-]}{[HOCl]} = \frac{k_7}{k_{-7}} \quad (9)$$

Eq. (9) defines the equilibrium constant for reaction (7), and equilibrium constant data are shown in Table 2.5. These values are dimensionless and thus are true equilibrium constant values. Fig. 2.2 shows dissociation of hypochlorous acid as a function of pH as presented by White (1972). Note that at the high pH relevant to this study, the dominant species is OCl^- .

Table 2.5: Equilibrium constant data for dissociation of hypochlorous acid at different temperatures (White, 1972)

T (°C)	$K_7 \times 10^8$
0	2
5	2.3
10	2.6
15	3
20	3.3
25	3.7

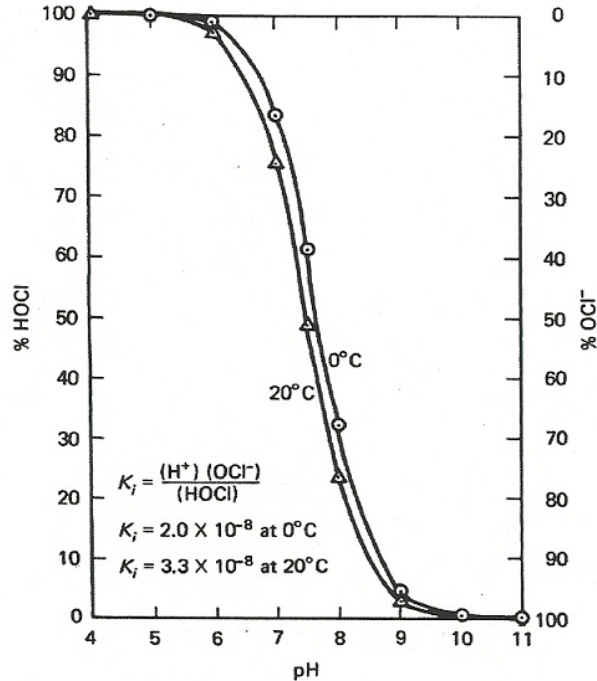
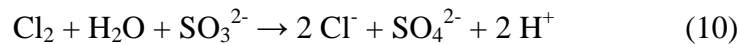


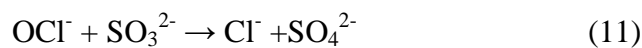
Figure 2.2: Dissociation of hypochlorous acid as a function of pH and T. Figure adapted from data by White (1972), used with permission from Wiley and Sons.

Reactions involving Sulfite and Chlorine

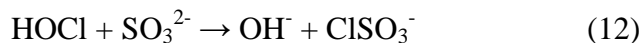
Dissolved Cl_2 reacts directly with sulfite to produce chloride and sulfate.



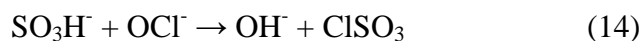
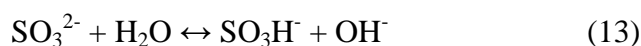
There are alternative mechanisms to explain how this reaction occurs. The study by Fogelman et al. (1989) indicates that there are two pathways. The first involves hydrolysis of the Cl_2 followed by the reaction of hypochlorite or hypochlorous acid with sulfite and the creation of a chlorosulfite intermediate. The first reaction pathway sees the sulfite ion oxidized by the hypochlorite ion as shown in Eq. 11. This reaction is not hydroxide inhibited.



The second reaction pathway takes place by either a single reaction or a combination of three. The first reaction in this pathway may account for the observed reaction rate by itself, and is believed to be hydroxide inhibited, is shown in equation 12.



The second (Eq. 13) and third (Eq. 14) reactions may take place in combination with Eq. 12 in order to produce the chlorosulfite intermediate (ClSO_3).



The empirical rate equation provided by Fogelman et al. (1989) (Eq. 15) to model these reaction pathways accounts for hydroxide ion inhibition; however, reaction rate is mostly independent of hydroxide concentration above 0.05 M.

$$k = \left(k_{11} + \frac{k_m}{[\text{OH}^-]} \right) [\text{SO}_3^{2-}] \quad (15)$$

k_{11} represents oxidation of sulfite by hypochlorite, and k_m is a first order rate constant representing the combined rate for either reaction 12, or reactions 12 through 14. Fogelman fitted kinetic data for equation 15, and the values of the parameters are shown in Table 2.6.

Table 2.6: Rate constants for the empirical rate law shown in Eq. 15 (Fogelman et al., 1989)

Name	Value
k_{11}	$(2.3 \pm 2) \times 10^4 \text{ M}^{-1}\text{s}^{-1}$
k_m	$450 \pm 30 \text{ s}^{-1}$

If it is assumed that the only reaction that is hydroxide inhibited is reaction (12), then it is possible to substitute the rate law for reaction (12) into Eq (15). The result of this is shown in Eq. (16).

$$k = \left(k_{11} + \frac{k_{-6}k_{12}}{k_6[OH^-] + k_{12}[SO_3^{2-}]} \right) [OCl^-][SO_3^{2-}] \quad (16)$$

k_{11} is the rate constant for reaction 11, k_6 and k_{-6} represent the rate constants for the forward and reverse of reaction 6, and k_{12} is rate constant for reaction 12. Fogelman's values for each rate constant in Eq. 16 are shown in Table 2.7.

Table 2.7: Values of rate constants used in Eq. 16 at 25°C and ionic strength of zero (Fogelman et al., 1988)

Reaction	Rate Constant
11	$(2.3 \pm 0.2) \times 10^4 \text{ M}^{-1}\text{s}^{-1}$
-6	$1.8 \times 10^3 \text{ s}^{-1}$
6	$3.0 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$
12	$(7.6 \pm 0.4) \times 10^8 \text{ M}^{-1}\text{s}^{-1}$

As a result of reactions (11) through (14), chlorine species react with sulfite at a faster rate when the pH is below 12.6 because sulfite reacts with HOCl at a rate four orders of magnitude greater than the reaction between sulfite and OCl⁻. Fogelman et al. (1989) state that the reaction between HOCl and sulfite (Eq. 12) is negligible above pH 12.6, as OCl⁻ is the only species present and available to react with the sulfite.

The chlorosulfite intermediate created by Eq. (12) and Eq. (14) goes on to react with water as shown in Eq. (17).



Yiin and Margerum (1988) studied this reaction in detail although a specific mechanism has not been proven. The rate constants for these reactions are shown in Table 2.8 as reported by Fogelman et al. (1989).

Table 2.8: Rate constants for formation of chlorosulfite intermediate and hydrolysis at 25 °C and ionic strength of zero (Fogelman et al., 1989)

Reaction	Rate Constant
12	$(7.6 \pm 0.4) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$
17	$(2.7 \pm 0.2) \times 10^2 \text{ s}^{-1}$

Another way of understanding the reaction of chlorine with sulfite (Eq. 10) was proposed by Roy and Rochelle (2004) who conducted experiments on chlorine absorption with sulfite solutions between pH 4.7 and 5.7. Their experiments showed that Cl_2 could react directly with sulfite without it being necessary to form a HOCl or OCl^- as an intermediate. The rate constants Roy and Rochelle found for reaction of sulfite and bisulfite with the different chlorine species are shown in Table 2.9.

Table 2.9: Rate constants for selected species reactions with sulfite at 25°C (Roy and Rochelle, 2004)

Chlorine Species	Rate Constant for reaction with sulfite
Cl_2 (Eq. 10)	$1.1 \times 10^9 \text{ L/mol}\cdot\text{s}$
HOCl (Eq. 12)	$7.6 \times 10^8 \text{ L/mol}\cdot\text{s}$
OCl^- (Eq. 11)	$2.3 \times 10^4 \text{ L/mol}\cdot\text{s}$

Roy and Rochelle point out that OCl^- is the dominant species at high pH and that decreasing pH to a point where HOCl is the dominant species dominates can cause an increased reaction rate. This is because Eq. (12) has a rate constant four orders of magnitude higher than that of Eq. (11). At still lower pH, Cl_2 is the favored species, and the favored reaction rate (for Eq. 10) is slightly higher still. However, taking into account uncertainties in the values, the rate constant for Eq. (12) is not necessarily higher than that of Eq. (10). Roy and Rochelle also mentioned that the reaction rates for chlorosulfite

intermediate formation (Eq. 12, 13, and 14) are much faster than the rate of formation of HOCl by chlorine hydrolysis.

Aqueous Chemistry of Sulfite

The total concentration of aqueous sulfite molecules is sometimes represented as S(IV), or the sum of SO_3^{2-} (sulfite) and HSO_3^- (bisulfite). Neta and Huie (1985) report the pK_a values for S(IV) species. For the transition from aqueous H_2SO_3 to HSO_3^- the pK_a value is equal to 1.86. For the transition from HSO_3^- to SO_3^{2-} the pK_a value is equal to 7.20. The pK_a data show that at the high pH with which this study is primarily concerned, S(IV) will be in the SO_3^{2-} form. At neutral and lower pH values, S(IV) is also present as HSO_3^- .

One particularly notable characteristic of the chemistry of aqueous sulfite is that sulfite can be oxidized into sulfate by chlorine and also by oxygen. Roy and Rochelle (2004) report that when chlorine and oxygen are being absorbed simultaneously, S(IV) oxidation depends on the concentrations of the respective gases as well as on the concentration of sulfite in solution. With Cl_2 fed at 275 ppm and O_2 fed at 14.5 mol % approximately three quarters of SO_3^{2-} oxidation was reported to be due to reaction of chlorine with SO_3^{2-} and the balance due to oxidation with oxygen. When only O_2 was fed at a concentration of 20.5 mol %, S(IV) oxidation took place at a rate of 0.068 mol/m² hr (mol of SO_3^{2-} formed per m² of interfacial area per hr). Roy and Rochelle also report that it is possible that Cl_2 catalyzes oxidation of SO_3 , although the observed behavior may only be due to SO_2 desorption.

From an operational standpoint SO_3^{2-} oxidation is important because fresh sulfite must be added as an experimental run is made. Additionally, chromatographic analysis of the scrubber solution samples must be analyzed relatively soon after they are taken to ensure an accurate measure of the sulfite concentration. If samples sit for hours before their analysis it could compromise experimental results.

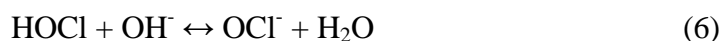
Summary of Reaction Pathways Relevant to This Process

The following reactions are significant to the study of a system composed of aqueous sodium sulfite and sodium hydroxide. There are basically two reaction pathways by which Cl_2 is consumed by sulfite in this system.

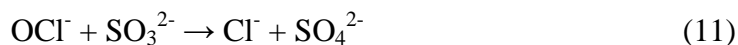
Pathway 1:



$$k_3 = (8 \pm 3) \times 10^8 \text{ L/mol s at } T = 30^\circ\text{C and } K_3 = 3.1 \times 10^{10}$$



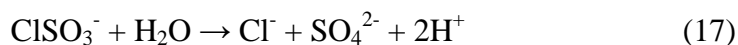
$$k_6 = 3.0 \times 10^9 \text{ L/mol s and } k_{-6} = 1.8 \times 10^3 \text{ s}^{-1} \text{ at } T = 25^\circ\text{C and } K_6 = 2.2 \times 10^6 \text{ L/mol at } T = 30^\circ\text{C}$$



$$k_{11} = (2.3 \pm 2) \times 10^4 \text{ M}^{-1}\text{s}^{-1}$$



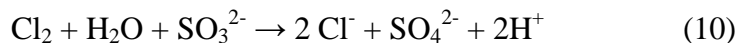
$$k_{12} = (7.6 \pm 0.4) \times 10^8 \text{ M}^{-1}\text{s}^{-1}$$



$$k_{17} = (2.7 \pm 0.2) \times 10^2 \text{ s}^{-1}$$

All reactions in pathway 1 are second order overall, but first order with respect to free chlorine (Cl_2 , HOCl , and OCl^-) and the liquid phase reactants (OH^- or SO_3^{2-}).

Pathway 2:



$$k_{10} = (1.1 \pm 0.3) \times 10^9 \text{ L/mol s at } T = 25^\circ\text{C}$$

In this pathway Cl_2 directly reacts with SO_3^{2-} . The values of the rate constants for reactions (3) and (10) are essentially equal after accounting for uncertainty values. The rate constant data suggests that the reaction pathways will compete when the concentrations of hydroxide and sulfite are on the same order of magnitude.

Cl_2 also can be scrubbed by using OH^- and water without the use of sulfite. When there is no sulfite present, reactions (2) and (3) control Cl_2 absorption with reaction (6) also playing a role. At a pH of 12 reactions (2) and (3) compete as neither is rate controlling.

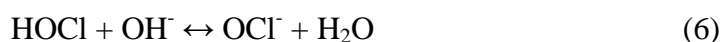


$$k_2 = (22.3 \pm 0.6) \text{ s}^{-1}, k_{-2} = 21.4 \pm 0.8 \times 10^3 \text{ M}^{-2}\text{s}^{-1} \text{ and}$$

$$K_2 = 3.94 \times 10^4 \text{ M}^2 \text{ at } T = 25^\circ\text{C}$$



$$k_3 = 8 \pm 3 \times 10^8 \text{ M}^{-1}\text{s}^{-1}, K_3 = 3.1 \times 10^{10} \text{ at } T = 30^\circ\text{C}$$



$$k_6 = 3.0 \times 10^9 \text{ M}^{-1}\text{s}^{-1} \quad K_6 = 2.2 \times 10^6 \text{ M}^{-1} \text{ at } T = 30^\circ\text{C}$$

Mass Transfer

The basic mass transfer flux equations based on the liquid and gas phases are shown in Eq. 19 (Geankopolis, 2003).

$$N_{Cl_2} = k_L (y - y_i) = k_g (x_i - x) \quad (19)$$

where k_L and k_g are the liquid and gas phase mass transfer coefficients respectively. y is the bulk phase gas concentration or fraction and y_i is the concentration or fraction at the gas-liquid interface. x_i is the concentration or fraction for the solute at the interface and x for the bulk. This equation can be expressed for Cl_2 absorption based on the gas phase partial pressure as in Eq. (20)

$$N_{Cl_2} = k_p (P_{Cl_2,b} - P_{Cl_2,i}) \quad (20)$$

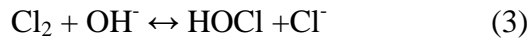
Where k_p is the mass transfer coefficient based on the gas phase, $P_{Cl_2,b}$ is the partial pressure of Cl_2 in the bulk, and $P_{Cl_2,i}$ is the partial pressure at the gas-liquid interface.

In this system, Cl_2 transport from the bulk gas into the liquid phase takes place over three key domains. First, the Cl_2 travels through the gas to reach an interfacial boundary where it can enter the second domain, a liquid boundary layer. Cl_2 must then migrate into the aqueous phase where it can undergo the final step in the process, chemical reaction. The reaction is a crucial step because it ensures that the Cl_2 in the aqueous solution will not reach equilibrium with the gas phase as long as equilibrium is not achieved. To understand the overall process, it is necessary to determine which step in the sequence supplies the dominant resistance to Cl_2 transport under various sets of conditions.

Information on mass transfer relevant to Cl_2 absorption into alkaline sulfite solutions is somewhat limited, coming mainly from the study by Roy and Rochelle

(2004). Complicating matters further is the fact that studies in literature with relevance to this one were concerned with absorption by randomly packed towers or wetted wall columns rather than structured packing.

For absorption of Cl₂ into NaOH aqueous solutions it seems generally agreed that mass transfer through liquid phase domain is the rate limiting step up for feeds of Cl₂ up to 64 mol%, a level above which Cl₂ solubility limitations come into play (Adams and Edmonds, 1937; Lahiri, 1983; Kister et al., 2008). Hikita et al. (1973) studied Cl₂ absorption into aqueous NaOH solutions as well. To describe liquid phase mass transfer he developed a “two reaction plane model” based on penetration theory and on the two-step reaction shown in Eq. (3) and (6).

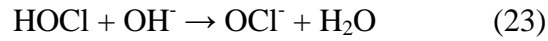
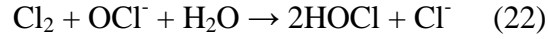


The model developed by Hikita et al. states that the ratio of the two equilibrium constants for reactions (3) and (6) determines the mechanism for chemical absorption and the liquid film profile for the system.

$$R = \frac{K_3}{K_6} \quad (21)$$

In the limiting case of $R = 0$, the reaction is understood to take place at a single reaction plane. In the other limiting case $R \rightarrow \infty$, the reaction is understood to take place at two reaction planes. In a system where Cl₂ is being absorbed into aqueous NaOH, the value of R is equal to 1.4×10^4 , which is a value high enough to justify the use of the two-plane approach presented by Hikita et al. (1973). According to this model the Cl₂ hydrolysis

reactions are understood to follow the two instantaneous irreversible reactions (21) and (22).



where reaction (22) takes place at the first plane and reaction (23), which is a modified version of reaction (6), takes place at the second plane. This two-plane approach means that the liquid phase concentration profile in the scrubbing liquor resembles those presented in Fig. 2.3.

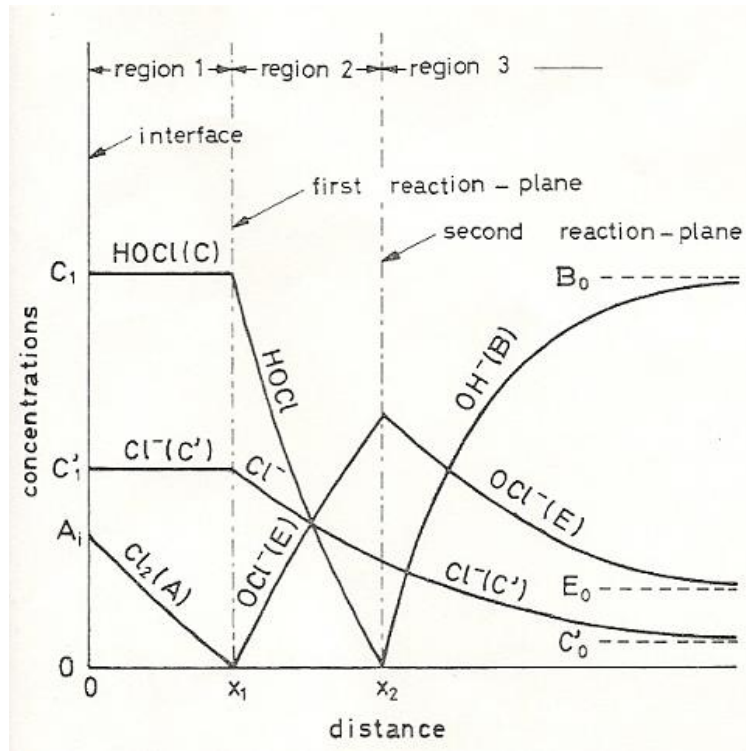


Fig. 2.3: Concentration profiles of species in an aqueous OH^- system absorbing Cl_2 (Hikita, 1973) used with permission from Elsevier.

One possibility raised by the two-plane reaction model is the potential for desorption of HOCl from the liquid phase as the concentration is high at the gas-liquid interface. HOCl is generally regarded as an air pollutant to be avoided. Desorption can occur in systems with a high gas phase mass transfer coefficient and low liquid mass transfer coefficient (Lahiri et al., 1983). If a column can be operated so that resistance is limited by gas phase mass transfer, then risk of desorption of HOCl will be minimal.

The role of sulfite must also be considered when studying this system. Roy (2004) studied absorption of Cl₂ into aqueous sulfite solution at pH between 4.7 and 5.7 using a wetted wall column. They concluded that for systems that had a sulfite concentration (in mol/L) ten times higher than the partial pressure of Cl₂ (in atm) mass transfer in the gas-phase would be the limiting step. Under this condition the chlorine reacts with sulfite as soon as it reaches the interface due to excess sulfite concentration. The partial pressure of Cl₂ at the interface approaches zero and Eq. (20) simplifies to

$$N_{Cl_2} = k_p P_{Cl_2,b} \quad (23)$$

Roy and Rochelle indicate that when Cl₂ concentration is high relative to sulfite concentration, mass transfer rate is limited by the flux of depleted sulfite to the interface. In this case, Cl₂ flux has a linear relationship with sulfite concentration.

$$N_{Cl_2} = k_{L,SO_3^{\circ}} [SO_3^{2-}]_b \quad (24)$$

where $k_{L,SO_3^{\circ}}$ is the liquid phase mass transfer coefficient based on the liquid phase bulk concentration of sulfite, $[SO_3^{2-}]_b$. In this situation there is little to no sulfite at the interface, and mass transfer is limited by how quickly sulfite can travel from the bulk liquid into the boundary layer where it undergoes fast chemical reaction with Cl₂. Roy

and Rochelle also indicated that at lower sulfite concentrations there is a contribution to the flux from the buffer used. They found that a succinate buffer enhanced Cl_2 hydrolysis, and at lower sulfite concentrations Cl_2 absorption was limited by the buffer-enhanced hydrolysis. This suggests that the caustic used with sulfite would enhance depletion of Cl_2 since OH^- also reacts with Cl_2 . At low sulfite concentrations such a system would approach caustic Cl_2 absorption similar to what was studied by Hikita et al. (1973) and Spalding (1962).

Information on correlation equations that can be used to predict mass transfer coefficients relevant to this system can be found in articles by Adams and Edmonds (1937), Ramamoorthi and Laddha (1987), and Rocha et al. (1996). Other information and correlations for specific column packings are available from manufacturers.

Heat Effects

Heat effects can be highly significant when designing a gas absorption column because temperature affects solubility, and changing temperatures can move the operating line of the column in way that is unfavorable. Heat effects can be caused by (1) the heats of reaction and mixing in the solution, (2) heat of vaporization or condensation from the solvent, (3) exchange of heat between the gas and liquid, and (4) transfer of heat to or from the surroundings (Kister et al., 2008).

EXPERIMENTAL METHODS

General Method

To gain the desired insights, the experiments were focused on variation of the following parameters.

- Cl₂ concentration and flowrate
- Air flowrate
- Recirculation rate of scrubbing liquor
- Sulfite concentration (including the condition of ‘zero sulfite’)
- Scrubbing capacity over time
- Packing height

Terminology

Some terms and definitions were developed in the experimental work plan as rubrics by which aspects of the process could be evaluated.

Chlorine Removal Efficiency – This refers to the percentage of chlorine removed from the air. For these studies, the overall chlorine removal efficiency was measured and reported:

$$\text{CRE} = [1 - (\text{g Cl}_2 \text{ in off-gas/batch})/(\text{g Cl}_2 \text{ fed/batch})]*100 \quad (25)$$

Scrubber Solution Capacity – The amount of chloride that the sulfite solution was able to trap and hold before the solution became spent or inefficient was calculated based on fraction of theoretical capacity:

$$\text{SSC} = (\text{moles Cl}^-/\text{mole SO}_3^{2-}) \quad (26)$$

Values for these definitions as determined from the experimental data are presented in the Experimental Results section.

Apparatus

A complete experimental procedure and a detailed equipment list are presented in Appendix F. What follows here is an abbreviated description. The safety cabinet apparatus that housed a cylinder containing pure Cl_2 is shown in Fig. 3.1. The overall experimental apparatus is displayed in Fig. 3.2, and the scrubber/tank assembly is shown in Fig. 3.3. In the figures, prefixes are used to denote the function of an item: F is a rotameter or flow meter, R is a pressure regulator, P is a pump, V represents a valve, and S represents an actuator valve used to open the solenoid valves in the chlorine cabinet. A key factor to note when considering the apparatus is the potential for corrosion due to the harsh chemicals being used in the process. Parts of the apparatus are exposed to “dry” and/or “wet” Cl_2 . Although indications from literature claimed that 304 stainless steel would hold up well when in contact with dry Cl_2 gas, there is a large amount of water throughout the system. The scrubbing liquor, at pH 12, contains potentially corrosive OH^- and hypochlorite (OCl^-). Thus, to avoid corrosion and degradation of the equipment, it was important to consider what materials were best to use in the construction of the apparatus. Some materials of construction will be noted here. An account of how materials and equipment held up will be presented in the results section.

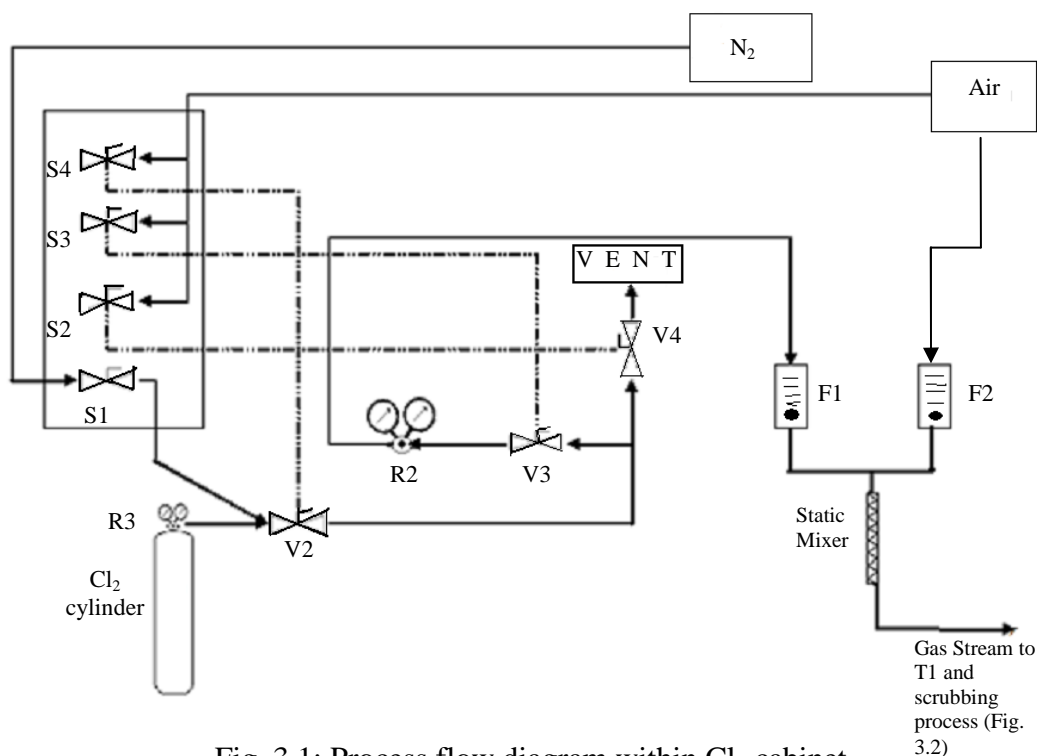


Fig. 3.1: Process flow diagram within Cl₂ cabinet

The Cl₂ gas cylinder was housed in a Gasguard cabinet, per university safety regulations. The main function of the cabinet was to safely isolate the Cl₂ cylinder. Process tubing in the cabinet was fabricated from Hastelloy C and monel, which are corrosion resistant alloys that provide protection from both dry and wet Cl₂. The Cl₂ gas exited the cylinder in the gas cabinet, traveled through stainless steel tubing and was mixed with house air. Rotameters were used to measure and control the flowrates of air (F2) and Cl₂ (F1) being fed to the process. The air and Cl₂ streams were mixed with a static convoluted mixer (0.5" diameter x 16" long) to thoroughly blend the streams before they traveled toward the overall process shown in Figure 3.2. The combined Cl₂/air gas feed entered the surge tank (T1), and from there it traveled up through the column and the packing. After being processed in the scrubber assembly (details of which can be seen in

Fig. 3.3) the effluent gas was vented in a laboratory hood. Just before being vented, a sample was split off to allow to the effluent to be analyzed by the Cl_2 detector. Outlet Cl_2 concentration was measured with an Ultima X/A Gas Monitor made by MSA (Cranberry Township, PA) which had a range 0.0 – 20.0 ppm. An integral diaphragm pump (P2) supplied by Ultima was used to ensure that a steady flowrate traveled from the effluent line through the detector to allow for reliable and consistent sampling.

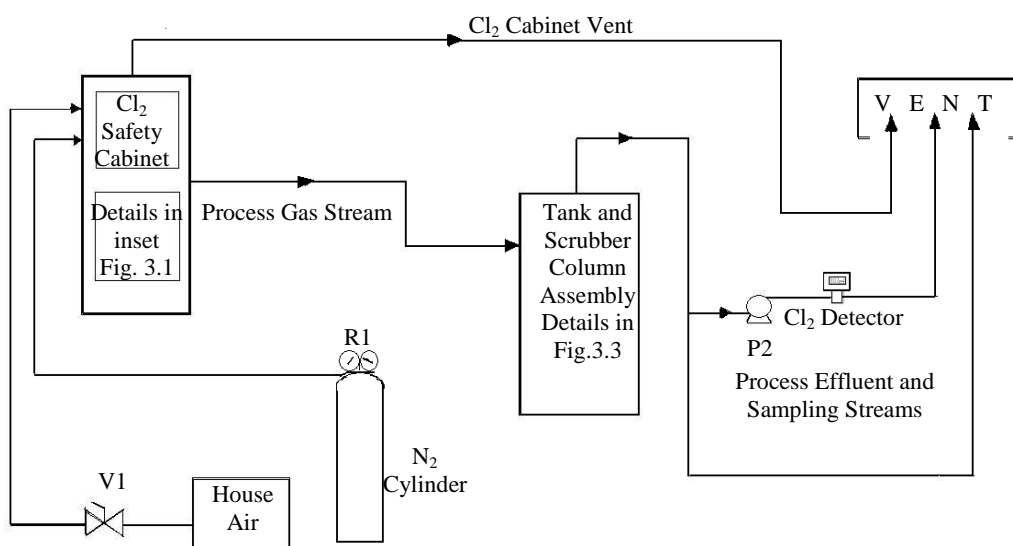


Fig. 3.2: Process Gas flow path through the experimental apparatus for this study

The Scrubber and Surge Tank Assembly are shown in greater detail Figure 3.3. The cylindrical tank (T1) used to store the scrubbing liquor was 304-L Stainless Steel. The column was constructed out of 304-L stainless steel pipe. During operation scrubbing liquor was pumped out of a port in the bottom of the tank to pump P1. After exiting P1 the liquor flow was split into an overpressure line and the feed line for the column. The flowrate for the liquor fed to the column was adjusted by the rotameter F5.

The excess flow was returned to T1 through the overpressure line. The overpressure line was useful as it was also the point of entry to the tank for the caustic solution and provided extra mixing for the tank. Valve V4 was set off the overpressure line, and through it scrubbing liquor samples could be taken. A $\frac{3}{4}$ hp pump was used for pump P1, and it was more than adequate to supply the flowrates required for the process.

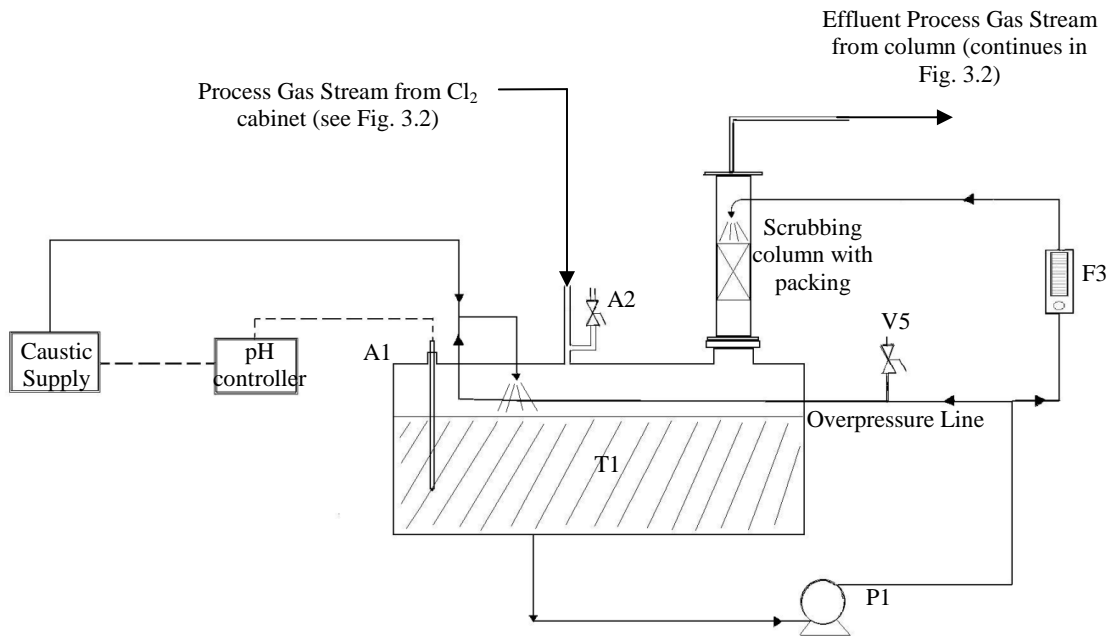


Fig. 3.3: Tank and Scrubber Assembly illustrating scrubbing liquor flow path

The packing used was a commercially available structured packing: Mellapak 750-Y made by Sulzer (Winterthur, Switzerland) (see fig. 3.4 and table 3.1). The material of construction for the packing was Hastelloy which was appropriate for this system as it is a corrosion-resistant alloy. Each section of packing was 8 $\frac{1}{4}$ inches in length, and 3 inches in diameter, allowing it to fit snugly inside the column. The sections of packing were “stackable,” which allowed for variation in the height of the packing. Most

experiments were run with only one section of packing, although runs were also made with two sections. When more than one section of packing was used, the segments were oriented so that the sheets of metal that make up the packing were not aligned, but rather they were staggered perpendicularly when viewed from a cross section. The manufacturer of the packing claimed that the scrubbing liquor would be distributed evenly across the packing very quickly. Despite this assurance, it was felt that it would be best to use a spray nozzle to ensure good distribution of the liquor. The nozzle was positioned so that its height relative to the top of the packing would cause the spray to reach the periphery of the packing but not hit the walls of the column and provide an even distribution of liquor across the top. Figure 3.4 shows a photograph of a unit of Mellapak 750-Y similar to the one used in this study.

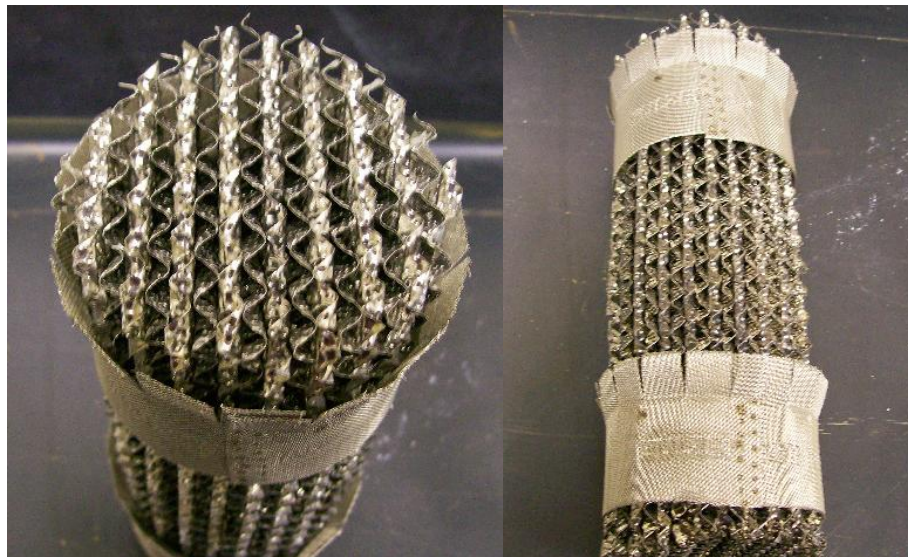


Figure 3.4: Photographs of a unit of Mellapak 750-Y that was used in this study

Some notable characteristics of Mellapak 750-Y are shown in Table 3.1

Table 3.1: Notable characteristics of Mellapak 750-Y (Sulzer; Kister et al., 2008)

Material of Construction:	Hastelloy C-276
Area:	750 m ² /m ³
% voids:	97
Liquid Loading:	0.2-200 m ³ /m ² hr
HETP:	approx. 0.2 m
Height per Element:	8 1/4 in. (208 mm)
Diameter:	3 in (80 mm)

Siminiceanu et al. (2001) also studied absorption using Mellapak 750Y. They found that the ratio of the effective and geometrical gas-liquid interfacial areas increased as Reynolds number of the liquid phase increases. Thus, depending on process conditions, the effective gas-liquid interfacial area for this study could be higher than the value shown in Table 3.1.

The exhaust tubing that lead to the vent sloped down slightly in order to allow any condensation to run out of the tubing. For most of the experiments this tubing was constructed of PVC, although an early incarnation was made of 304L stainless steel. At one point in the stainless steel effluent tubing, some condensation managed to pool up. Small holes developed in the tubing, presumably because the condensate absorbed some Cl₂ gas, which was converted to aqueous HCl. Although this took place within the relatively safe confines of a gas hood, and the exhaust typically contained only low concentrations of Cl₂, a similar apparatus within a plant setting should be designed to avoid allowing any stagnant liquid to accumulate anywhere within the system.

A Thermocouple made by Omega Monogram (Stamford, CT) was used to provide temperature measurements of the scrubbing liquor inside the tank. A pressure gauge was included on the tank, but it never read any discernible pressure difference compared to the atmosphere during experimental operation, so it was removed. Ion chromatography was used to analyze the scrubber liquor samples. Standard solutions of chloride, sulfite, and sulfate were prepared prior to each run to allow comparison to experimental samples.

Experimental Procedure

For a more detailed operating procedure, consult Appendix F. The scrubbing solution was prepared and added to the tank by filling the tank to 265 liters and adding the mass of sodium sulfite appropriate to achieve the desired concentration. The pH control solution was prepared from NaOH and water and was added through the pH controller to the scrubbing solution until a pH of 12 was achieved.

With the solution prepared and in the tank and the pump on, the house air was turned on and adjusted to the normal air flowrate or approximately 25 L/min assuming $T = 25^{\circ}\text{C}$). A check was done on the tubing leading to the diaphragm pump to ensure that it was clear of water. The diaphragm pump was then turned on to ensure that sufficient flow is being pushed through the Cl_2 detector. The pump remained on for the duration of the experiment.

A check was conducted to ensure that all portals and seals were closed and to ensure that there were no gas leaks in the system. Once it was verified that conditions would be safe to begin operation, the final part of the startup took place: Cl_2 gas flow was started by opening the cylinder with a wrench and then opening the appropriate solenoid

valves in the safety cabinet. The Cl_2 flow was adjusted quickly to the desired setting with F1. The time that Cl_2 flow began was recorded.

To maintain the desired pH for the experiment, it was necessary to mix up fresh solutions of caustic and replace what had been used. This procedure was performed in the same manner as the first caustic addition; 200 g of NaOH was added to flasks containing 2L of water, resulting in 2.5 M concentration. The caustic in the flasks was then fed automatically by the pH. Mixing was achieved by adding the caustic in the overpressure line where excess liquor flowed back into the tank T1.

Experimental data were recorded by hand into a laboratory notebook. Parameters to be monitored and recorded were outlet Cl_2 concentration, inlet air and Cl_2 flowrate, temperature, pH, liquor flowrate, and NaOH consumption. The time at which each reading was taken was recorded as well. Samples of the scrubbing liquor were taken into a plastic container from V4 so that they could be analyzed using ion chromatography. The chromatography analysis had to be performed relatively soon after the sample was taken, preferably within an hour. This was decided after the sulfite in some liquor samples was severely decomposed by oxidation after being left out overnight.

When it was time to shut down, the first thing to be done was to shut off Cl_2 flow by closing the rotameter, shutting the appropriate valves in the Cl_2 cabinet, and then closing the Cl_2 cylinder itself with a wrench. Air flow was allowed to continue, as was recirculation flow of liquor. Meanwhile a thorough N_2 purge was performed to clear Cl_2 from the tubing in the gas cabinet to prevent corrosion. Flow of caustic was turned off, and the line through the pH controller was rinsed out with water to avoid corrosion. The

diaphragm pump was turned off, and the tank was emptied. The tank was filled again with tap water and emptied again to rinse it clear of chemicals and rust.

EXPERIMENTAL RESULTS

Detailed data from the experiments are compiled in Appendix A. Results will be presented in this section to show the influence of the following process variables:

1. Sulfite concentration
2. Inlet Cl₂ concentration
3. Inlet ambient air flowrate
4. Recirculation rate
5. Packing height
6. Capacity of the scrubbing liquor for absorption after extensive operation (high gravity scrubbing liquor)

Analysis of Scrubber Performance

Experimental results were analyzed using mass balances. Inlet gas streams were monitored with rotameters, and the Cl₂ cylinder was weighed. Composition of scrubbing liquor was analyzed with ion chromatography (IC) that gave concentrations of chloride, sulfite, and sulfate. The effluent gas stream was analyzed using a detector that allowed detection of chlorine concentration to the nearest 0.1 ppm between 0.0 and 20.0 ppm. A Chlorine Removal Efficiency (CRE) of greater than 99.5% had to be achieved for this system to be considered satisfactory.

Experimental conditions were set primarily around the operating conditions DOE indicated would be standard for operation at Savannah River Site. The main design stipulation was that the column was required to be able to process Cl₂ at a rate of approximately 0.53 kg/hr. Initial experimental runs established that the column would be

able to provide a CRE superior to the 99.5% removal required for successful operation at the MOX facility. Table 4.1 shows the results of a run made with a starting Na_2SO_3 concentration of 0.1 M, with the ‘targeted’ Cl_2 flowrate of 0.53 kg/hr.

Table 4.1: Experimental Results of 0.1 M Sulfite Concentration Run; Cl_2 flow at 0.53 kg/hr, ambient air flow at 6.4 L/min, liquor flow at 1.7 gpm

minutes	Cl_2 outlet concentration (ppm)	Cl_2 outlet flowrate (kg/hr)	Fraction of Cl_2 in Effluent	CRE (%)
0	~	~	~	~
6	0.2	5.4E-05	1.0E-04	99.99
9	0.4	1.1E-04	2.0E-04	99.98
10	0.5	1.4E-04	2.6E-04	99.97
13	0.6	1.6E-04	3.1E-04	99.97
18	0.7	1.9E-04	3.6E-04	99.96
26	0.7	1.9E-04	3.6E-04	99.96
32	0.7	1.9E-04	3.6E-04	99.96
37	0.6	1.6E-04	3.1E-04	99.97
42	0.5	1.4E-04	2.6E-04	99.97
44	0.5	1.4E-04	2.6E-04	99.97
49	0.4	1.1E-04	2.0E-04	99.98
62	0.2	5.4E-05	1.0E-04	99.99
64	0.2	5.4E-05	1.0E-04	99.99
68	0.1	2.7E-05	5.1E-05	99.99
71	0.1	2.7E-05	5.1E-05	99.99

Table 4.1 demonstrates that the scrubber satisfies the MOX facility’s CRE requirements, with all CRE values well above 99.5%.

Analysis of Chemistry

Next it was desirable to gain an understanding of the roles of the two scrubbing agents being utilized, Na_2SO_3 and NaOH . A run that was particularly enlightening to this end was made with a starting amount of 835 g Na_2SO_3 (or half the amount originally proposed for use in the MOX process by DOE). During this experiment the column was

operated with Na_2SO_3 and aqueous NaOH both present, and then with only NaOH after the Na_2SO_3 was spent. The starting mass of sulfite of 835 g corresponds to 530 g of the SO_3^{2-} ion or a sulfite concentration of 0.025 M. Figure 4.1 shows IC data for the consumption of sulfite for this ‘half sulfite’ run.

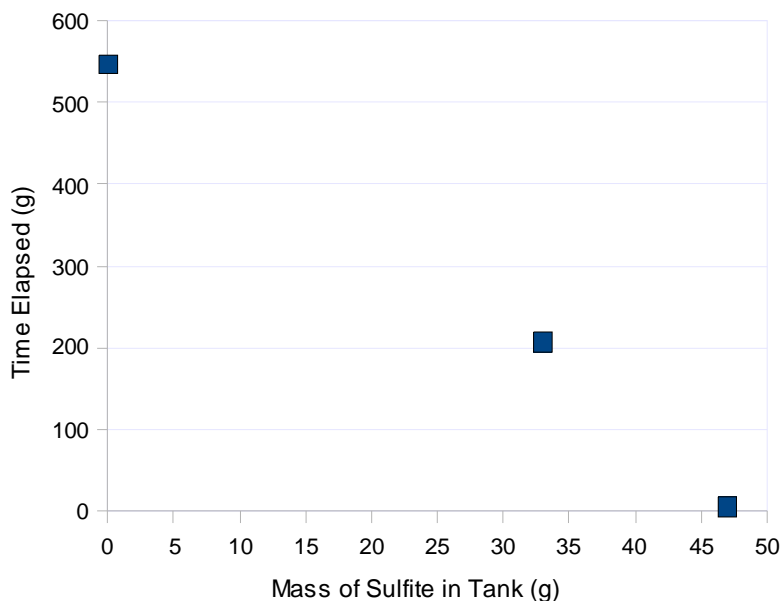


Fig. 4.1: Sulfite in Tank vs Experimental Time Elapsed for the 0.025 M Sulfite Run

Fig. 4.1 indicates that the sulfite was spent after about 45 minutes of operation at the standard Cl_2 flowrate (0.53 kg/hr). A chromatography sample taken at the beginning of the run indicated a total sulfite mass of 546 g in the tank. Considering this as a spot check, the chromatography value was about 3% over the value as determined by the mass inputs. This and other spot checks indicated that the IC data provide accurate tracking for sulfite. For more information on how chromatography data were calculated and interpreted, the reader is directed to Appendix C. To allow better understanding of reagent consumption and to allow comparison between different runs it was important to

normalize reagent concentrations by using chloride concentrations as the independent variable. This technique is illustrated in Fig. 4.2, which utilizes chloride IC data to compare the moles of sulfite in the tank to Cl_2 being added to the tank through the scrubbing process.

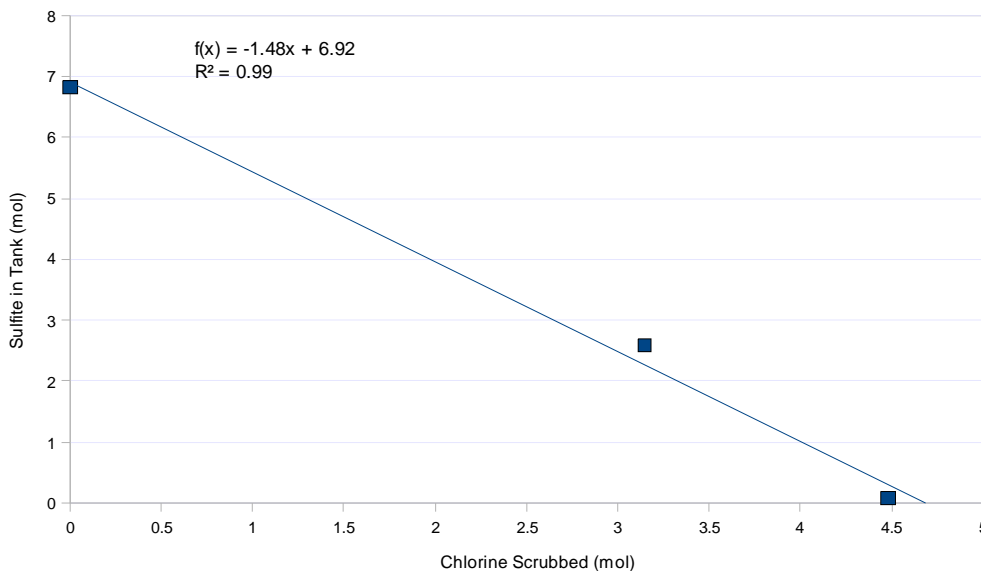


Fig 4.2: Sulfite consumption for half sulfite run as a function of Cl_2 absorbed. Results indicate that 1.5 moles of sulfite were consumed per mole Cl_2 scrubbed.

A regression performed on the IC data indicated that about 1.5 moles of sulfite were required to scrub a single mole of Cl_2 . A linear correlation between chlorine scrubbed and sulfite was observed in other experiments as well. Fig. 4.3 shows the consumption of sulfite relative to the Cl_2 being scrubbed by the column for another run. This run was designated as ‘high salt’ as it was made primarily to investigate the performance of the column after extended use, and this aspect will be discussed more in the ‘Extended Use/High Salt Concentration’ section.

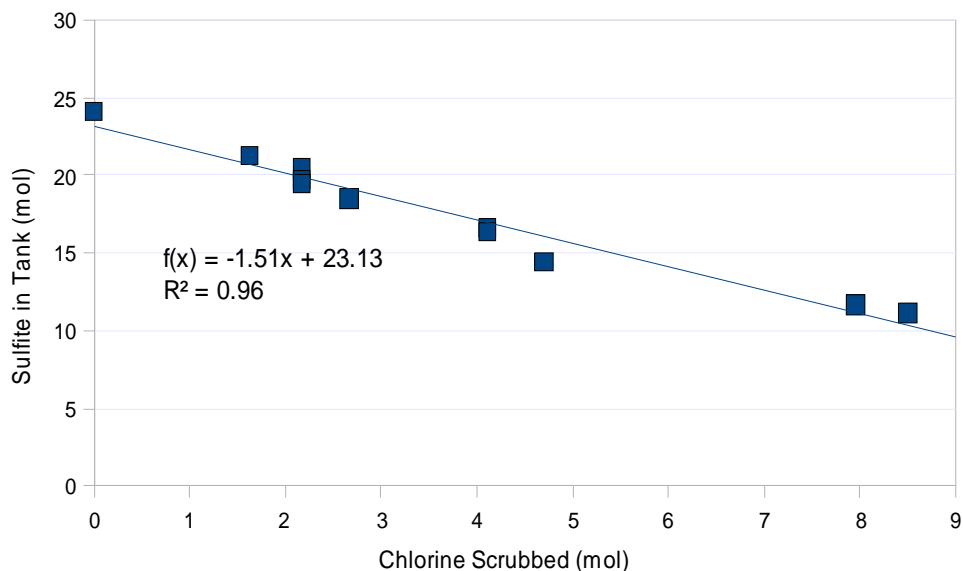


Fig 4.3: Sulfite consumption in 2nd High Salt Run; results are similar to those in Fig 4.2, with 1.5 moles sulfite consumed per mole of Cl₂ scrubbed.

The regression performed on the sulfite consumption data for the ‘high salt run’ (Fig. 4.3) showed good agreement with the data presented for the half sulfite run (Fig. 4.2). Again, this regression indicated that about 1.5 moles of SO₃²⁻ were consumed for every mole of Cl₂ scrubbed.

According to the stoichiometry presented in the literature review, the reaction of Cl₂ with SO₃²⁻ (Eq. 10) requires one mole of sulfite to react with each mole of Cl₂ being scrubbed. The results presented in Fig. 4.2 and 4.3 show that sulfite was consumed at a rate higher than the 1:1 ratio anticipated, with the observed figure being approximately 1.5:1. This higher ratio is due to sulfite being consumed and transformed into sulfate via its reaction with O₂ from the air in the gas feed. Using a wetted wall column, Roy and

Rochelle (2004) determined that when Cl_2 and O_2 are being absorbed simultaneously, approximately one fourth of the consumption of sulfite was due to oxidation of sulfite. They also report that sulfite oxidation increases as sulfite concentration increases due to the greater amount of sulfite present at the gas-liquid interface. Roy and Rochelle also mention that it is possible that Cl_2 may catalyze the oxidation of sulfite at higher sulfite concentrations (such as those being considered in this study). A study of Mellapak 750Y by Siminiceanu et al. (2008) also mentions that the kinetics of sulfite oxidation are not fully understood and studies have been inconsistent with their findings. Thus, a significant amount of sulfite being consumed by this undesirable oxidation reaction is not unexpected.

Analysis of NaOH consumption data also yields insight into the roles of the NaOH and Na_2SO_3 as scrubbing agents for Cl_2 in this system. Fig. 4.4 displays results from the half sulfite run for the time period before the sulfite in the solution was spent (0-45 minutes according to Fig. 4.1). The data were based on the quantity of caustic solution being added by the pH controller.

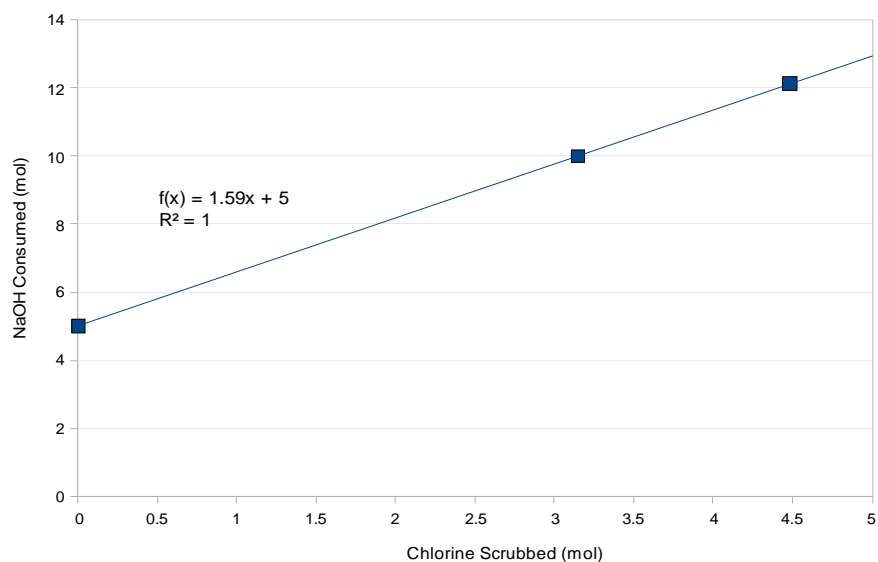


Fig. 4.4: NaOH consumed as a function of chlorine scrubbed for the half sulfite run with sulfite present.

A regression was again performed on the data, which indicated that NaOH was consumed at a rate of about 1.6 mole of NaOH per mole of Cl_2 . The NaOH consumption results of a run made with a ‘standard’ starting concentration of 0.05 M are displayed in Fig. 4.5.

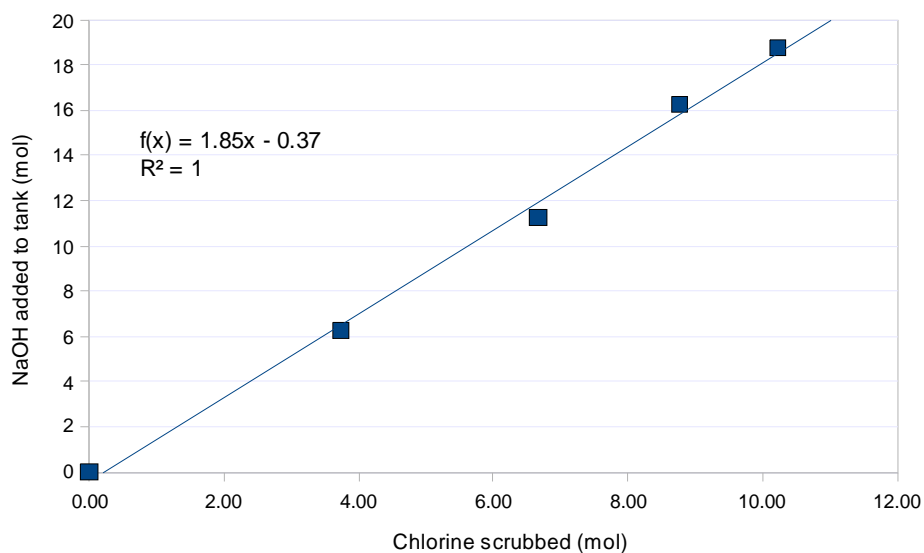


Fig. 4.5: NaOH consumption in a run where sulfite was present at a starting concentration of 0.05 M

The regression performed on the data in Fig. 4.5 indicates that about 1.8 moles of NaOH were consumed per mole of Cl₂ scrubbed.

NaOH consumption data for the high salt run (earlier examined in Fig. 4.3) are shown below in Fig. 4.6; this plot indicates that about 2.2 moles NaOH were consumed per mole of Cl₂ scrubbed. This value is higher than the values from with Fig. 4.5 and 4.6.

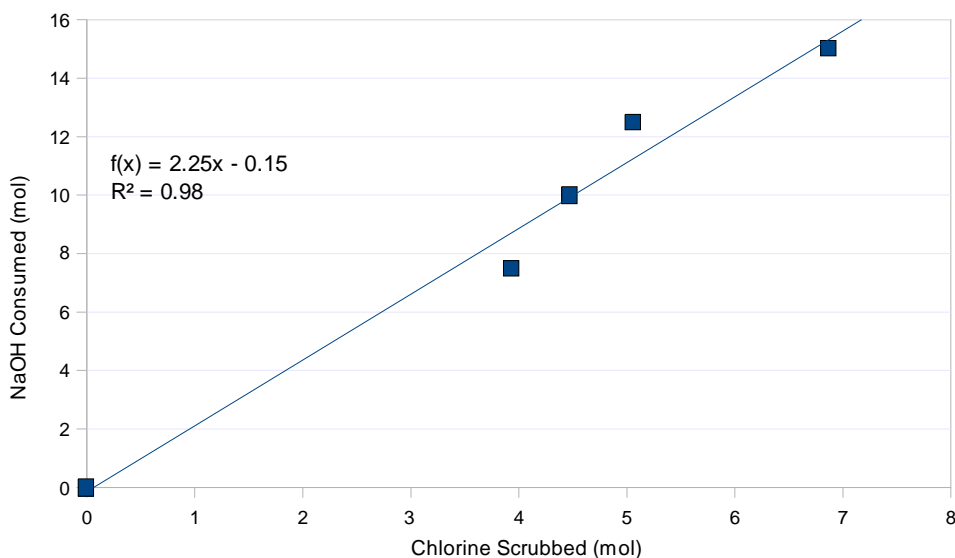


Fig. 4.6: NaOH consumption in High Salt Run 2. Sulfite was present for these results.

So far only results with sulfite present in the scrubbing liquor have been considered. In Fig. 4.1 the IC results for the half sulfite run show that sulfite was completely consumed after about 45-50 minutes of operation, but operation of the column was continued after this point. This change provides a good opportunity to compare how the chemistry of the system changes in the absence of sulfite. NaOH consumption data for the half sulfite run are presented in Fig 4.7.

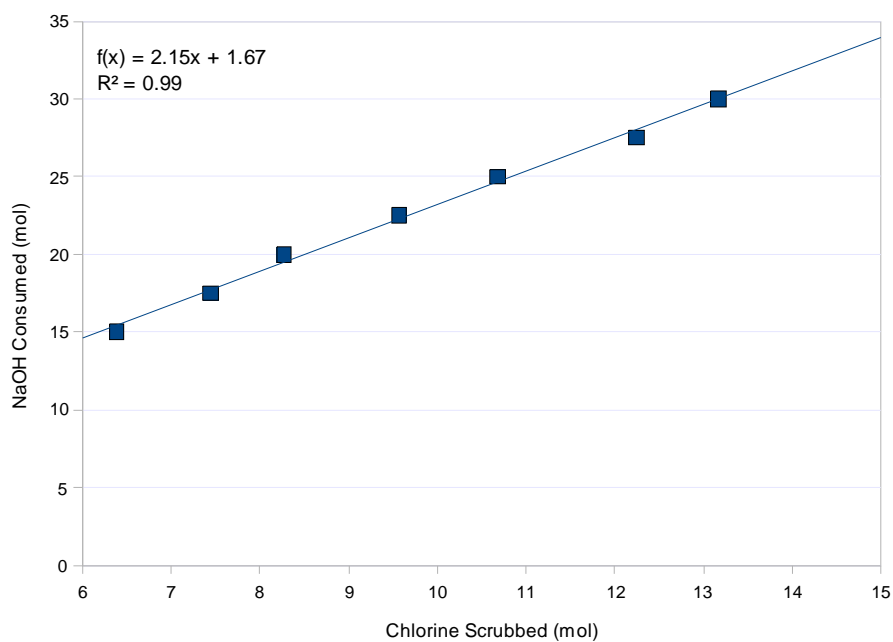


Fig. 4.7: Consumption of NaOH consumed after sulfite in the scrubbing liquor was spent for the half sulfite run

The regression for the data in Fig. 4.7 indicates that about 2.2 moles of NaOH were added per mole of Cl_2 scrubbed. This is an increase in the rate of NaOH consumption by about 35% compared to the time when the sulfite concentration in the liquor was near 0.025 M, although the higher rate may be due to the pH controller lagging behind conditions in the surge tank (Fig. 4.4). Data from a run made with no sulfite in the scrubbing liquor for the duration of the experiment displayed similar results in Fig. 4.8.

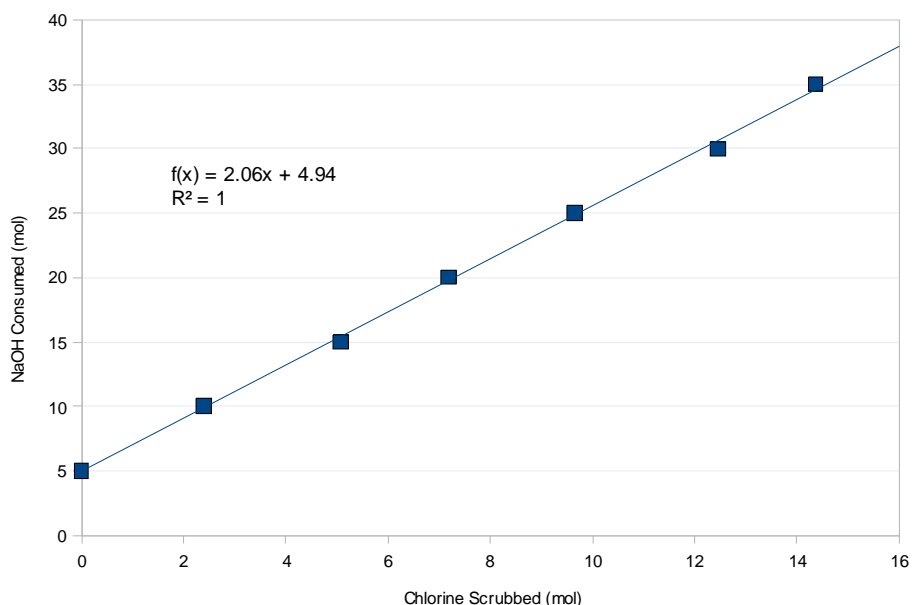


Fig. 4.8: NaOH consumption for a run where no sulfite was present for the duration of the experiment.

The regression for the data in Fig. 4.8 show that approximately 2.0 moles of NaOH were required to scrub each mole of Cl_2 . A summary of the regression values for sulfite and NaOH consumption is presented in Table 4.2.

Table 4.2: Average moles of reagent consumed per mole Cl_2 scrubbed. Values are presented for the mixed reagent system and for the system where only NaOH was present as a scrubbing agent

Reagent	Sulfite & NaOH system	NaOH only system
sulfite	1.5 (Fig. 4. 2, 4.3)	~
NaOH	1.9 (Fig. 4. 4, 4.5, 4.6)	2.1 (Fig. 4.7, 4.8)

The regression values presented in Table 4.2 allow insight into the fundamental chemistry taking place. Again, the sulfite was consumed at a 1.5:1 Cl_2 to SO_3^{2-} ratio due to the oxidation of sulfite. The NaOH consumption values presented by Table 4.2 also provide valuable insight into the chemistry of the system. Stoichiometry of the reaction pathways involving sulfite indicate that two moles of NaOH would be consumed in

processing a single mole of Cl_2 and maintain the pH of the solution. The reaction pathway involving Cl_2 hydrolysis and reaction with caustic also theoretically required 2 moles of NaOH per mole Cl_2 .

Results of Table 4.2 indicate that the NaOH consumption in the aqueous sulfite system was slightly lower than the expected at an average of about 1.9:1 mol of NaOH per mol of Cl_2 scrubbed. In runs where no sulfite was present, an average of 2.1 moles of NaOH were consumed per mole of Cl_2 . In the run where no sulfite at all was used (Fig. 4.8) NaOH consumption was observed to be 2 moles NaOH to 1 mole of Cl_2 which is what is expected from the stoichiometry. It is worth noting again that these values come from the NaOH added by the pH controller. It is possible that using controller data to monitor OH^- consumption caused some inconsistency in the data because the control lags slightly behind real-time scrubbing of Cl_2 . Average values from the experimental results are consistent with the theoretical stoichiometric requirements shown in the sulfite pathways as well as the hydrolysis pathway presented in the literature review, as both sulfite and hydrolysis both require that 2 moles of NaOH are consumed per mole of Cl_2 scrubbed.

Chromatography data for chloride allows an estimate of how much of the Cl_2 scrubbed was converted into Cl^- and HOCl/OCl^- once in solution. Chromatography results for Cl^- were subtracted from the total amount of Cl_2 scrubbed, and the difference was used to estimate the approximate amount of OCl^- in the tank. Figure 4.9 uses chromatography results from the 'no sulfite' run. The figure shows that when there is no

sulfite present (and all absorption is taking place through the hydrolysis pathway), OCl^- is present at levels slightly lower than Cl^- .

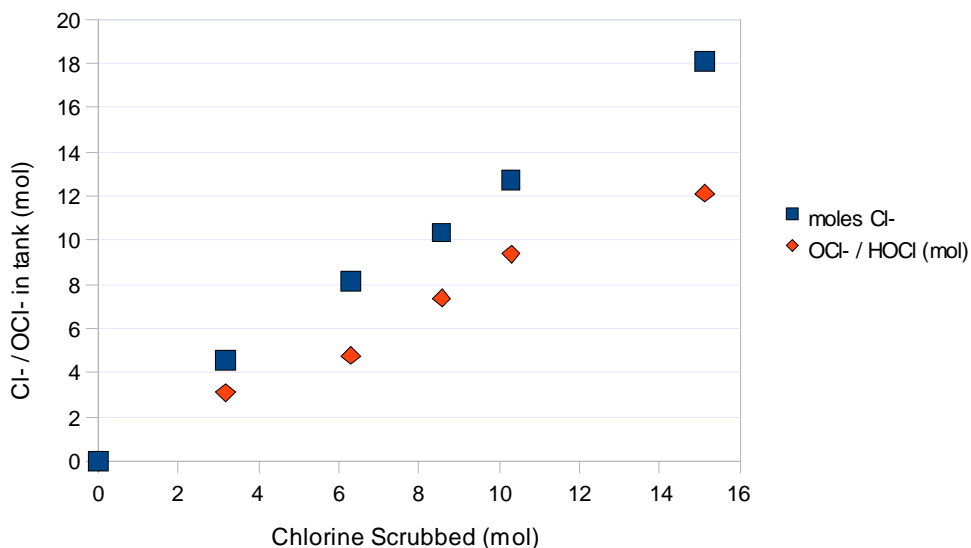


Figure 4.9: Cl^- and OCl^- data for the No Sulfite Run

A similar analysis of data from the half sulfite run is presented in Figure 4.10. Again, this run is of particular interest as it had sulfite present for the early part of the experiment, and after that the system was scrubbing Cl_2 only through the hydrolysis pathway. In Figure 4.10 the points where sulfite was present were at less than 5 moles Cl_2 scrubbed, or the first three points on the plot. The fact that Cl^- concentration rises steadily in this part of the experiment where sulfite is present while concentration of OCl^- stays relatively small indicates that the sulfite pathway is favored when there is sulfite present. Concentration of OCl^- stays relatively low because OCl^- is consumed by sulfite through reaction (11). Figure 4.10 for the data points above 5 moles Cl_2 scrubbed where the concentration of OCl^- begins to rise in a manner similar to that in Figure 4.9. This

suggests that the hydrolysis pathway becomes dominant as the sulfite concentration approaches zero.

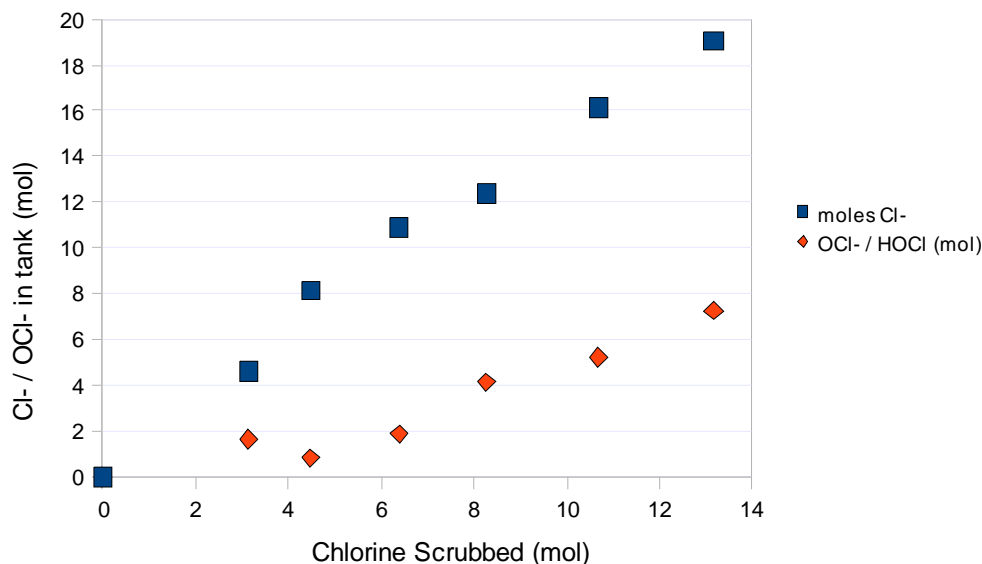


Figure 4.10: Cl^- and OCl^- data for the Half Sulfite Run; Concentration of OCl^- remains relatively low while sulfite is present in the system (up to 5 mol on the x-axis).

In summary, sulfite was consumed at a ratio over the 1:1 mole of sulfite per mole of Cl_2 , and NaOH was added to maintain constant pH at a rate roughly equal to the 2:1 ratio expected. Concentrations of OCl^- were observed to be relatively low compared to Cl^- concentrations. This suggests that the reaction of Cl_2 with sulfite (Eq. (10) in the literature review) is favored over the hydrolysis pathway when sulfite is present in significant concentrations. As sulfite concentration drops close to zero, the hydrolysis pathway involving reactions (2), (3), and (6) in the literature review section becomes dominant.

Scrubber Solution Capacity and Operational Effects of Sulfite Concentration

The point at which the Na_2SO_3 in the scrubbing liquor becomes spent for this system was of interest to DOE in this study. The regression data presented in Table 4.2 indicate that about 13.6 mol (1.7 kg) of sodium sulfite are required to scrub the 10.3 mol (0.72 kg) of Cl_2 in the design-case run at standard conditions. Recall that Scrubber Solution Capacity was defined by Equation (26) in the Experimental Method section as

$$\text{SSC} = (\text{moles } \text{Cl}^- / \text{mole } \text{SO}_3^{2-}) \quad (26)$$

According to the data presented in Table 4.2 and the definition presented in Equation the SSC is equal to 1.3. The point where sulfite was spent (shown in Figure X.1) provides a unique opportunity to consider how sulfite affects the ability of the scrubber to remove Cl_2 compared to a system using NaOH only.

Selected effluent stream Cl_2 concentrations for the half sulfite run (0.025 M starting sulfite concentration) are tabulated in Table 4.3. After startup of the experiment, Cl_2 concentrations in the effluent stream rose slowly and then settled at values between 0.5 and 0.8 ppm. Concentrations then jumped near the 50 minute mark settling at 1.7 ppm. From the chromatography results shown in Fig. 4.1 it is known that the sulfite of the solution was spent at around the 45-50 minute mark. The fact that other flowrates and other operating conditions were held constant for the duration the experiment supports the conclusion that the jump in outlet concentration was due to the exhaustion of the sulfite.

Table 4.3: Effluent Cl₂ Concentrations for the Half Sulfite Run; Cl₂ concentrations in the effluent were stable but then doubled near the time the sulfite was spent.

minutes	Cl ₂ outlet concentration (ppm)
0	0
3	0
9	0
13	0.2
15	0.4
20	0.5
24	0.7
26	0.8
33	0.8
35	0.8
46	0.8
47	0.9
53	1.6
57	1.7
64	1.7
67	1.7
70	1.6

A similar phenomenon was observed in another experiment, whose results are tabulated in Table 4.4.

Table 4.4: Effluent Cl₂ concentrations for the ‘double packing height’ experiment: Cl₂ concentrations were constant at or near zero until the sulfite was spent, at which point Cl₂ increased to a value of 2 ppm.

time min	Cl ₂ outlet concentration (ppm)
0-135	0 – 0.1
139	1
140	1.3
146	2.4
148	2.3
150	2.1
151	2
153	1.9

This experimental run was primarily concerned with the packing height (a topic that will be discussed later), and it used a starting sulfite concentration of 0.05 M, which was twice as high as the half sulfite run examined in Table 4.3. With an extra section of packing, the column scrubbed practically all the Cl₂ fed for the first 135 minutes of operation. After that, the effluent Cl₂ concentrations increased to a value around 2 ppm. While the rise in Cl₂ concentration was accompanied by a drop in flowrate of the total air, the process conditions were simply being returned to conditions that were present about 20 minutes earlier, so it is believed that the increase was associated with the sulfite having been spent.

These experiments indicated that the exhaustion of the sulfite causes a slight increase in the Cl₂ concentration in the effluent stream. Sudden 1-2 ppm rises were observed in the effluent, which works out to be about 0.01 g/hour of Cl₂, or a decrease in CRE of about 0.001 - 0.002%. This change in effluent concentration is small from an operational standpoint considering that the CRE is still well above the 99.5 % required for successful operation of the column in the MOX facility.

The fact that CRE values were still nearly as high after the sulfite was spent raises an obvious question: why not just use sodium hydroxide alone as the scrubbing agent if the benefit provided by sulfite is only 2 ppm lower Cl₂ in the exhaust? DOE chose to include sodium sulfite as a scrubbing reagent for this system in part to prevent unwanted side reactions. Unwanted products from Cl₂ hydrolysis can include sodium chlorate, sodium chloride, sodium chlorite, and excess hypochlorous acid. As mentioned in the literature review, it is possible for hypochlorous acid and other potential pollutants to be

stripped into the effluent gas stream. Sodium chlorite can decompose to sodium chloride and oxygen, which can cause unwanted heat generation as well as foaming of the scrubbing liquor and inhibit mass transfer within the column. Hypochloric acid, hypochlorite, and sodium chlorite are corrosive and it is desirable to keep their concentrations to a minimum. Hypochlorite can also cause problems for wastewater treatment systems. Using sulfite to react with Cl_2 through reaction (10) mitigates the risks associated with these unwanted side products (Lennon, 2005).

Mass Transfer

As discussed in the literature review section, the rate of Cl_2 absorption into aqueous sulfite can be limited by gas phase or liquid phase mass transfer, depending on operating conditions. Gas phase limited mass transfer would be a desirable characteristic for this process as mass transfer through the gas phase is generally faster than mass transfer through the liquid phase by two orders of magnitude (Geankopolis, 2003). Whether gas phase control could or would apply to this system was unclear. The ratio of sulfite concentration to Cl_2 partial pressure was lower for most experimental conditions in this study, closer to 1:1 (M:atm) compared to the 10:1 criterion reported by Roy and Rochelle (2004).

The traditional method of Cl_2 absorption by aqueous NaOH is agreed to be limited by liquid phase mass transfer under a wide variety of conditions (Roy and Rochelle, 2004; Kister, et al., 2008; Hikita, 1962). When the rate of mass transfer is limited by the liquid phase, Roy states that absorption is a function of sulfite

concentration (Eq. 24). If the system is rate-limited by gas phase mass transfer, absorption is independent of sulfite concentration (Eq. 23).

As demonstrated in Table 4.3 in the previous section, a slight increase in Cl_2 effluent concentration was noted as concentration of sulfite started at 0.025 M and progressively dropped to zero. The increase of effluent Cl_2 concentration was small relative to the inlet feed of Cl_2 , but the results suggest that at these low to intermediate sulfite concentrations, mass transfer is limited by the liquid phase. This relationship would be consistent with what Roy and Rochelle found: that Cl_2 absorption was proportional to sulfite concentration at intermediate concentrations, with hydrolysis taking over as sulfite was consumed.

At higher sulfite concentrations where mass transfer is more likely to be gas-phase limited, it was not possible to discern any trend in the data (as seen in Table 4.1, for example). No trend is apparent because the effluent Cl_2 concentrations were very low under most conditions tested, including conditions where there was no sulfite present and the rate of mass transfer was known to be limited by the liquid phase (Table 4.5 in the next section, for example). Therefore, data are inconclusive as to establishing the circumstances under which gas phase-controlled mass transfer becomes rate limiting for this process.

Recirculation Rate

Recirculation rate was varied during each experimental run to determine its effect on CRE. The run made with no sulfite in the scrubbing liquor is a particularly good case to consider because a changing sulfite concentration could not have obfuscated the

results. Results with different levels of liquid recirculation rate or liquid loading for the ‘no sulfite’ run are tabulated in tables 4.5.1, 4.5.2, and 4.5.3. The corresponding recirculation rates for these tables are 1.8 gpm ($81 \text{ m}^3/\text{m}^2 \text{ hr}$), 1.2 gpm ($54 \text{ m}^3/\text{m}^2 \text{ hr}$), and 0.6 gpm ($27 \text{ m}^3/\text{m}^2 \text{ hr}$) respectively.

Table 4.5.1: Cl_2 outlet concentration (ppm) at 1.8 gpm ($81 \text{ m}^3/\text{m}^2 \text{ hr}$ liquid loading). Average and median concentrations were 1.1 and 1.2 ppm respectively.

time (min)	Cl_2 outlet concentration (ppm)
7	0.2
8	0.4
9	0.6
11	0.7
11.5	0.8
12	0.9
14	1
15	1.1
17	1.3
20	1.2
23	1.3
26	1.4
29	1.4
31	1.4
33	1.4
39	1.4
44	1.4
51	1.4

Table 4.5.2: Effluent Cl_2 concentrations for 1.2 gpm liquor flowrate ($54 \text{ m}^3/\text{m}^2 \text{ hr}$ liquid loading). Average and median concentrations were 1.5 and 1.5 ppm respectively.

time (min)	Cl_2 outlet concentration (ppm)
53	1.4
54	1.5
59	1.5
64	1.5

Table 4.5.3: Effluent Cl₂ concentrations for 0.6 gpm (27 m³/m² hr liquid loading). Average and median concentrations were 8.2 and 6.6 ppm respectively.

time (min)	Cl ₂ outlet concentration (ppm)
65	1.5
66	1.9
67	3.5
69	6.2
70	9
71	14.6
72	14.9
73	15
74	13
79	9.3
84	7.9
89	5.6
94	5
99	9
104	7.1

Mean and median values for the outlet Cl₂ concentrations were calculated as well. The Cl₂ mean and median values for the 1.8 gpm flowrate (81 m³/m² hr liquid loading) were 1.1 and 1.3 ppm, respectively. For the 1.2 gpm flowrate (54 m³/m² hr) mean and median values were 1.5 and 1.5 ppm, respectively. When the flowrate was 0.6 gpm (27 m³/m² hr) mean and median values were 8.9 and 8.5, respectively. Also of interest is that the standard deviation for the concentration data points at the 1.8 gpm flowrate was 0.4 ppm, while the standard deviation for the 0.6 gpm flowrate was 5 ppm. So, considering these results, it may be concluded that a lower recirculation rate can cause a decrease in performance. Additionally, noting the higher variance at the lower flowrate it appears that the CRE is less stable at the lower flowrate. This agrees with the study by

Siminiceanu et al. (2001) that found that effective gas-liquid interfacial area increases as Reynolds Number of the scrubbing liquor increases. However, even with the poorer performance at the low flowrate, the column still operated well within DOE requirements for operation in the MOX facility. Although Mellapak 750-Y can accommodate a high range of liquid loading up to $200 \text{ m}^3/\text{m}^2\text{hr}$, loading values above $100 \text{ m}^3/\text{m}^2 \text{ hr}$ (2.2 gpm for this column) did not provide any discernible benefit for this process (Harden, 2007).

Based on the results observed in these experiments, it is recommended that the liquor flowrate through the packing be set between 50 to $100 \text{ m}^3/\text{m}^2 \text{ hr}$ (1.2 to 2.2 gpm for this system) if the column is being operated with one section of packing. Higher liquid loading values up to $100 \text{ m}^3/\text{m}^2 \text{ hr}$ provide higher CRE, while the lower flowrate still allows for a high and stable CRE value while also allowing the potential for monetary savings through the use of a smaller pump and lower electricity costs.

Inlet Gas Flowrate

Data for comparison of air flowrates were taken from the run made with no sulfite so that the results would be independent of sulfite concentration. Selected results with two different air flowrates were examined while inlet Cl_2 concentration and recirculation liquor rate were held constant at 0.53 kg/hr and 0.6 gpm, respectively. Data for these different air flowrates are tabulated in Table 4.6.

Table 4.6: Ambient air flowrates comparison 1; Cl_2 feed and liquor flowrates held constant. The lower air flowrate provided superior performance.

Air Flowrate (rotameter)	Air flowrate liters/min	Cl_2 outlet conc. in ppm (mean)	Cl_2 effluent conc. ppm (median)	Cl_2 flowrate moles/min (mean)	Cl_2 flowrate moles/min (median)
0.9	12	3.3	2.7	1.6 E-06	1.3 E-06
1.9	24	9.0	8.4	8.9 E-06	8.4 E-06

The Cl₂ effluent flow was about five times higher for the higher ambient air flowrate than it was for the lower flowrate. Another comparison of inlet air flowrates was made, this time including a higher ambient air flowrate along with a Cl₂ flowrate that was slightly higher (0.74 kg/hr). Data for this comparison are presented in Table 4.7.

Table 4.7: Ambient air flowrates comparison two; little change in outlet concentration is observable. Cl₂ and liquor flows were held constant.

Air Flowrate (rotameter)	Air flowrate liters/min	Cl ₂ outlet conc. in ppm (mean)	Cl ₂ effluent conc. in ppm (median)	Cl ₂ flowrate moles/min (mean)	Cl ₂ flowrate moles/min (median)
1.9	24	6.6	4.5	6.5 E-06	1.7 E-06
2.9	37	4.5	0.9	4.7 E-06	1.4 E-06

This time the Cl₂ outlet flowrate was slightly higher for the lower flowrate although the difference in scrubber performance was not large. Based on these results, a smaller gas flowrate through the column such as the one in Table 4.6 (12 liters per minute) seems to improve scrubber performance slightly, apparently due to the higher residence time of the gas stream as well as a greater concentration gradient driving force. This is because the higher residence time provided by a lower flowrate allows for a greater amount of time for the Cl₂ to be in contact with the scrubbing liquor. For installation in the MOX facility, note that a very low non-chlorine gas flowrate through the system is not desirable since a higher Cl₂ concentration could lead to greater corrosion and degradation of the process equipment and potentially cause safety hazards.

Packing Height

While most experiments were done with one section of 8 ¼ inch high, 3 inch diameter packing, the column was tested with an extra section of packing to evaluate the

effect of packing height on scrubber effectiveness. With the second section of the packing, the total packing height was 16 ½ inches. The main run to test the effect of a second section of packing revealed some interesting findings (tabulated results were displayed earlier in Table 4.4). The standard Cl₂ flowrate corresponding to 0.53 kg/hr was used for the first 100 minutes of operation, and the Cl₂ detector read 0.0 ppm for the entire experiment.

In the early part of the double packing height experiment, operating conditions were made to mimic those that had caused the Cl₂ detector to go over the maximum reading of 20 ppm, in previous experiments. Even under these conditions the detector still read 0.0 ppm. Even after dropping the liquor flowrate down to 0.4 gpm, and then to 0.2 gpm, the Cl₂ detector still measured 0.0 ppm Cl₂. The inlet Cl₂ flowrate was adjusted to 0.7 kg/hr, near the maximum allowed by the Cl₂ rotameter, at the 100 min mark of operation. With the liquor flowrate set at only 0.4 gpm, the detector continued to indicate no outlet Cl₂ in the effluent stream for the next half hour of operation. As shown in Table 4.4, the Cl₂ concentration suddenly rose to an average value of 1.9 ppm after about 135-140 minutes of operation. Again, this sudden rise is believed to correspond to the point at which the sulfite in the scrubbing liquor became spent.

Selected data for the double packing height experiment are tabulated in smaller increments in Table 4.8

Table 4.8: Selected data for the ‘double packing height’ run corresponding to time after the sulfite solution was spent. Average Cl₂ reading was 1.9 ppm; standard deviation of data points was 0.45 ppm.

Experimental Time Elapsed (min)	Cl ₂ inlet flow (kg/hr)	Cl ₂ outlet reading (ppm)
139	0.70	1
140	0.74	1.3
146	0.74	2.4
148	0.74	2.3
150	0.74	2.1
151	0.74	2
153	0.74	1.9
156	0.74	1.9
157	0.74	1.8

Table 4.9: Selected data for the ‘no sulfite run’ that used a single section of packing. Average Cl₂ effluent concentration was 12.7 ppm and standard deviation was 5.6 ppm.

Experimental Time Elapsed (min)	Cl ₂ inlet flow (kg/hr)	Cl ₂ outlet reading (ppm)
134	0.79	5
138	0.79	12.1
142	0.79	17.1
146	0.79	16.7

Table 4.9 shows Cl₂ effluent concentrations for the ‘no sulfite run’ when the column was being run with a similar Cl₂ flowrate and a similar liquor flowrate, but with only one section of packing. In Table 4.9 we see that the ‘no sulfite run’ had an average Cl₂ effluent concentration of 12.7 ppm for the data with the single section of packing. The double packing height data in Table 4.8 show a more stable Cl₂ effluent concentration than the data from the single packing unit run (despite the single packing run being at a slightly higher liquor flowrate). The standard deviation of Cl₂ concentration readings are 0.45 and 5.6 ppm respectively.

Again comparing the data in Tables 4.8 and 4.9, we note that outlet concentration is about six to seven times higher in the experiment with the shorter packing height. Even though CRE is somewhat higher with the additional packing, the comparable data from the single packing height run would still be well within acceptable operating conditions for DOE. Based on experimental results, it is recommended that the single 8 ¼ inch high section of packing would be adequate for this system. Additional packing height would be recommended only if an effluent Cl₂ concentration of 0.0 ppm were desired.

Extended Use/High Salt Concentration

DOE specified that it would be desirable to be able to make five scrubbing runs before the operators are required to drain the tank and add fresh scrubbing liquor. It was desirable to assess whether there would be any change in column performance if a batch of scrubbing liquor were used repeatedly instead of being replaced after each use. To simulate the conditions of scrubbing liquor that had not been replenished after several runs, the column was operated with a high salt concentration. NaCl was added to the scrubbing liquor to simulate having made already made about five runs at DOE's standard operating conditions. Cl⁻ concentration was 0.8% by weight and SO₄²⁻ was 2.5% in this high salt liquor. Sulfite concentration was set at the standard 0.05 M specified by DOE, and the experiment was run using the same procedure as those that used fresh scrubbing liquor. Selected results are shown in Table 4.10

Table 4.10: Extended Use Analysis: Effluent Concentrations for the High Salt Run 1; Cl₂ flowrate at 0.53 kg/hr, liquor recirculation rate at 1.8 gpm, and starting sulfite concentration of 0.05M. Average and median outlet Cl₂ concentration was 0.7 ppm and standard deviation 0.5 ppm

minutes	Cl ₂ effluent conc. (ppm)
1	0.1
18	0.2
22	0
34	0.1
35	0.7
36	1.1
38	1.8
40	1.3
42	0.7
43	0.9
46	0.6

Tabulated data for a run made under similar operating conditions that used ‘fresh’ scrubbing liquor is displayed in Table 4.11 below.

Table 4.11: Extended Use Analysis: Effluent Concentrations for a starting sulfite concentration 0.05 M. Cl₂ flowrate at 0.53 kg/hr and liquor recirculation rate of 1.5 gpm, and starting. Average and median outlet Cl₂ concentration was 0.4 and 0.5 ppm respectively and standard deviation was 0.2 ppm

minutes	Cl ₂ outlet conc. (ppm)
11	0.1
12	0.2
15	0.4
32	0.4
41	0.4
44	0.4
47	0.4

Comparing the results from the two runs, the high salt run had an average outlet concentration of 0.7 ppm while the average concentration for the run made with fresh

scrubbing liquor was 0.4 ppm. After accounting for the standard deviations these values are not significantly different. Data from lower liquor flowrates, however, did demonstrate a drop in column performance with high salt concentration in the liquor. Running the column at 0.6 gpm caused the Cl₂ effluent concentration to exceed 20 ppm after about one minute of operation. Running the column at 1.0 gpm caused the effluent concentration to rise to around 15 ppm. Under the same conditions with 'fresh' scrubbing liquor and 0.05 M starting sulfite concentration the column had performed better.

Therefore it is concluded that there is some drop in performance when the scrubber is run with a high salt concentration, especially at lower liquor flow rates. Roy and Rochelle experimented with adding salt to the scrubbing solution and found that there was no effect on the rate of Cl₂ absorption in sulfite solution (Roy and Rochelle, 2004). Therefore it is likely that the slightly diminished performance of the column is due to the higher density and slightly higher viscosity of the high salt scrubbing liquor, and the fact that Mellapak 750-Y creates less gas-liquid interfacial area at lower Reynolds numbers (Siminiceanu et al., 2001). If the column were to be used five times consecutively as DOE had desired it would be necessary to maintain a higher flowrate. A liquor flowrate of at least 1.8 gpm (or 80 m³/m²hr) would be recommended in this case.

It is also noteworthy that NaOH, NaCl, OCl⁻ and other chemicals present in the apparatus are corrosive, and it is desirable to keep their concentrations low to avoid degradation of the process equipment. Also, the MOX facility has a regulatory

concentration limit of 5 g of chloride per liter for wastewater. Thus the scrubbing liquor should be changed at regular intervals.

Role of pH

The pH for this study was specified to be 12, and for the vast majority of the time the system was operated at $\text{pH} = 12 \pm 0.1$. The pH of the system was allowed to drift lower during some experiments, as far down as pH 10, and there was no consistent difference in CRE observed. pH was also as high as 12.5 at times, and there was also no discernible difference in performance. The chemistry of sulfite stays the basically the same down to the pK_a value (pH 7.2) at which point HSO_3^- becomes the dominant species over SO_3^{2-} . Considering that Spalding (1962) reported the rate of absorption through hydrolysis remains roughly the same between pH values of 4 and 11, it seems likely that the system could be operated effectively down to about a pH of 7.2. It is unclear how the system would perform below this value as the chemistry of the system changes. Regardless of the pH specified for the process, some method of pH control or buffer is necessary because reaction of Cl_2 with caustic and water causes the pH to drop rapidly.

Heat Effects

Temperature of the scrubbing liquor in the recirculation tank was monitored with a thermocouple to assess thermal effects associated with this system. Heats of reaction and mixing were anticipated to be the main sources of heat effects for this column. Cooling was not expected to be needed for this column based on initial Aspen simulations, so none was provided. The temperature of the liquor in the tank was

observed to increase by about 5 °C over the course of the longer experiments due to the net exothermic effects of the reactions taking place in the scrubber. However, no apparent decrease in performance was noted. Unless the system is altered or scaled up greatly for use in another facility it will be unnecessary to cool the scrubbing liquor.

Equipment Performance/Additional Operational and Safety Concerns

In the first experiments performed, a substantial amount of rust accumulated in the tank over the course of a run. The scrubbing liquor would become noticeably brown in color, and some sediment would be obviously present when the tank was emptied after an experiment. After a few experiments had been performed however, the amount of rust that would typically accumulate over the course of a run became noticeably smaller. It is believed that over the course of operation, some of the iron present on the inside surface of the tank had been stripped out of the stainless steel, leaving a relatively inert surface layer of nickel and chromium.

The process feed line became significantly corroded in a number of spots in the effluent line (all between the cabinet and the tank), always on the bottom part of the tube. It is believed that this occurred due to a buildup of condensation from water vapor diffusing back up the process feed line from the tank. This accumulation of water absorbed Cl₂ which in turn, was converted to HCl. A brown sludgy substance was found inside the stainless tubing, which was replaced with PVC tubing.

The valves and tubing in the gas cabinet also showed signs of corrosion. This is somewhat surprising, as dry Cl₂ is not normally corrosive to stainless steel. It seems likely that humidity and condensation from the liquid in the column combined with the

chlorine present also contributed to this corrosion during down time. If a system such as this is operated intermittently, it will be advisable to do repeated nitrogen purges of all lines and to use isolation valves in each section.

In early runs of the column a demister pad made of 18-8 stainless steel was included in the top of the column, but it quickly degraded after being exposed to the small amount of wet Cl_2 in the effluent. Since the presence of a small amount of liquid water in the effluent was inconsequential, the remains of the demister were removed and not replaced.

CONCLUSIONS

This study investigated a scrubber that has the ability to abate a gas stream containing 0.53 kg/hr of chlorine using aqueous sodium sulfite at pH 12 with a minimum Chlorine Removal Efficiency (CRE) of 99.5% or greater. The scrubber system provided excellent overall performance with respect to this criterion, delivering CRE of 99.95% under the vast majority of conditions tested. It is possible to operate the scrubber effectively using aqueous Na₂SO₃ and NaOH as scrubbing agents, or just NaOH by itself, but the inclusion of Na₂SO₃ provides operational benefits. Aqueous sulfite is thought to prevent unwanted side reactions and prevent desorption of hypochlorous acid. The reaction of sulfite with Cl₂ is favored over hydrolysis as a reaction pathway when sulfite is present in significant concentrations. Liquid phase mass transfer is believed to be the rate limiting step for this system; conditions for gas-phase control could not be established conclusively. Scrubber Solution Capacity (mole of Cl₂ processed per mole of SO₃ consumed) was determined to be 1.3. The main operating conditions that were found to be detrimental to column performance were a liquor recirculation rate that was too low and a total gas flow through the column that was too high. A gas flowrate of 10-12 L/min through the system is recommended for use. Increasing liquor recirculation rates provided slightly improved CRE up to 2.2 gpm (100 m³/m²hr). Liquid loading between 50 and 100 m³/m²hr (1.2 - 2.2 gpm for this column) is recommended for operation. Increasing the packing height improved scrubber performance, but the column met performance requirements with a single 8¼ inch section of Mellapak 750-Y. The

system experienced a slight increase in temperature over the course of operation, but thermal effects were not detrimental to column performance.

APPENDICES

Appendix A

Selected Experimental Data

Table A.1: Selected data from half sulfite run (0.025 M starting sulfite concentration)

Time (minutes)	Liquor Flow (gpm)	Air Flow (L/min) at STP	Cl ₂ flowrate (g/min)	Cl ₂ outlet conc. (ppm)	total moles Cl- in tank (mol)	total moles sulfite in tank	NaOH added to tank (mol)
0	1.8	24	530	0	0.26	6.82	5
3	1.8	24	530	0			
9	1.8	24	530	0			
13	1.8	24	530	0.2			
15	1.8	24	530	0.4			
20	1.8	24	530	0.5			
24	1.8	24	530	0.7			
26	1.8	24	530	0.8			
33	1.8	24	530	0.8	3.52	2.59	10
35	1.8	24	530	0.8			
46	1.8	24	530	0.8			
47	1.8	24	530	0.9	6	0.08	12.15
53	1.8	24	530	1.6			
57	1.8	24	530	1.7			
64	1.8	24	530	1.6			
67	1.8	24	530		7.94	~	15
70	0.6	24	530				
71	0.6	24	530	2.8			
72	1	24	530	OVER			
73	1	24	530	5.8			
74	1	24	530	5.4			
75	1	24	530	7.3			
76	1	24	530	7.5			
77	1	24	530	8.3			
78	1	24	560	5.7			17.5
79	1	24	515	3.7			
83	1	24	515				
87	1	24	515		9.01	~	20

Table A.1: Half Sulfite Run cont.

Time (minutes)	Liquor Flow (gpm)	Air Flow (L/min) at STP	Cl ₂ flowrate (g/min)	Cl ₂ outlet conc. (ppm)	total moles Cl- in tank (mol)	total moles sulfite in tank	NaOH added to tank (mol)
90	1	37	515	OVER			
94	1.4	24	515				
96	1.4	24	515	2			
97	1.4	24	515	1.8			
98	1.4	37	515	1.7			
99	1.4	37	515	1.8			
100	1.4	37	515	1.9			
101	1.4	37	515	3.9			22.5
104	1.4	37	515	4.5			
106	1.4	37	515	5.4			
108	1.4	12	515	5.5			
109	1.4	12	515				
110	1.4	12	515	1.9			
113	1.4	12	515	1.4	11.65	~	25
115	1.4	12	515	1.4			
117	1.4	24	760				
119	1.4	24	760	2.2			
121	1.4	24	760	2.2			
122	1.6	24	760	1.9			
124	1.6	24	760	1.9			
125	1.6	24	760				27.51
127	2.4	24	690	1.6			
129	2.4	24	690	1.7			
131	2.4	24	690	1.7			
132	1.8	24	515				
133	1.8	24	515		13.72	~	30.01
135	1.8	24	515	1.3			
137	1.8	24	515	1.2			
139	1.8	24	515	1.1			
141	1.8	24	0				
147	1.8	24	0		13.72	~	32.51

Table A.2: High Salt Run 2

Air Flow cont @ 24
L/min at STP
Cl₂ flow const @ 0.53
kg/hr at STP

minutes	Liquor Flow	Cl ₂ outlet conc (ppm)	total moles Cl ⁻ in tank	total moles sulfite in tank	NaOH added to tank (mol)
0	1.8	0.0			0
6	1.8	0.0	55.58	16.85	
6	1.8	0.0			
9	1.8	0.0			
12	1.8	0.0	74.77	21.27	
12	1.8	0.0			
15	1.8	0.0			
17	1.8	0.0	76.39	20.43	
17	1.8	0.0			
22	1.8	0.0	76.89	19.73	
22	1.8	0.0			
27	1.8	0.0	78.93	19.51	
27	1.8	0.0			
29.75	1.8	0.0			
34.75	1.8	0.0	79.01	18.53	
34.75	1.8	0.0			
41.75	1.8	0.0			7.5
42.75	1.8	0.1			
44.75	1.8	0.1	81.75	16.62	
44.75	1.8	0.1			
49.75	1.8	0.1	81.95	16.36	
49.75	1.8	0.1			
51.75	1.8	0.1			10
52.75	0.6	0.0			
53	1.8	OVER			

Table A.A.2: High Salt Run 2 cont.

minutes	Liquor Flow	Cl ₂ outlet conc (ppm)	total moles Cl ⁻ in tank	total moles sulfite in tank	NaOH added to tank (mol)
62.75	1.8		85.12	14.41	
62.75	1.8				
64.75	1				12.5
66.75	1	2.2			
67.75	1	4.4			
68.75	1	5.1			
69.75	1	5.5			
70.75	1	6.8			
71.75	1	7.4			
72.75	1	13.1			
73.75	1	19.5			
74.75	1	3.0			15
75.75	1	0.7			
76.75	1.8	0.5			
78.75	1.8	0.4			
79	1.8				
79.75	1.8	0.2			
80.75	1.8	0.2	85.81	11.67	
82.75	1.8				
83.75	1.8	0.1			
84.75	1.8		88.72	11.16	

Table A.3: No Sulfite Run

minutes	Liquor Flow (gpm)	Air Flow Rate (L/min) at STP	Cl ₂ flowrate (g/hr)	Cl ₂ outlet conc (ppm)	total moles chloride in tank	NaOH added (mol)
7	1.8	24	530	0.2		5
8	1.8	24	530	0.4		
9	1.8	24	530	0.6		
11	1.8	24	530	0.7		
11.5	1.8	24	530	0.8		
12	1.8	24	530	0.9		
14	1.8	24	530	1		
15	1.8	24	530	1.1		
17	1.8	24	530	1.3		
20	1.8	24	530	1.2		
23	1.8	24	530	1.3		
26	1.8	24	530	1.4		
29	1.8	24	530	1.4		
31	1.8	24	530	1.4		
33	1.8	24	530	1.4		
39	1.8	24	530	1.4		10
44	1.8	24	530	1.4	4.6	
51	1.8	24	530	1.4		
53	1.2	24	530	1.4		
54	1.2	24	530	1.5		
59	1.2	24	530	1.5		
64	1.2	24	530	1.5		
65	0.6	24	530	1.5		
66	0.6	24	530	1.9		
67	0.6	24	530	3.5		
69	0.6	24	530	6.2		
70	0.6	24	530	9		
71	0.6	24	530	14.6		15
72	0.6	24	530	14.9		

Table A.3: No Sulfite Run cont.

minutes	Liquor Flow (gpm)	Air Flow Rate (L/min) at STP	Cl ₂ flowrate (g/hr)	Cl ₂ outlet conc (ppm)	total moles chloride in tank	NaOH added (mol)
73	0.6	24	530	15		
74	0.6	24	530	13		
79	0.6	24	530	9.3		
84	0.6	24	530	7.9		
87	0.6	24	530		8.1	
89	0.6	24	530	5.6		
94	0.6	24	530	5		
99	0.6	24	530	9		
104	0.6	24	530	7.1		20
105	0.6	37	530			
106	0.6	24	530	>20		
107	0.6	24	530	10.3		
108	0.6	24	530	6.7		
109	0.6	12	530	6.8		
110	0.6	12	530	4.7		
112	0.6	12	530	3.5		
114	0.6	12	530	2.9		
116	0.6	12	530	2.7		
118	0.6	12	530		10.3	
119	0.6	12	530	2.4		
120	0.6	12	530	2.4		
121	0.6	12	530	2.3		
122	0.6	12	530	2.3		
124	0.6	24	530	4.5		
129	0.6	24	530	4.7		
132	0.6	24	530	4.8		
133	0.6	24	530			
134	0.6	24	760			25
138	0.6	24	760	12.1		
139	0.6	24	760		12.7	
142	0.6	24	760	17.1		
146	0.6	24	760	16.7		
147	0.6	24	760			

Table A.3: No Sulfite Run cont.

minutes	Liquor Flow (gpm)	Air Flow Rate (L/min)	Cl2 flowrate (g/hr)	Cl2 outlet conc (ppm)	total moles chloride in tank	NaOH added (mol)
151	0.6	24	760	1.9		
155	0.6	24	760	1.5		
159	0.6	24	760	1.3		
161	0.6	24	760			30
162	0.6	24	760	1.1		
164	0.6	24	760	1.1		
165	0.6	37	530			
169	0.6	37	530	1		
174	0.6	37	530	0.8		
177	0.6	37	760	0.8		
180	0.6	37	760	0.9		
187	0.6	37	760	11.9		35
189	0.6	37	0		18.1	35

Table A.4: Double Packing Height Run

Cl₂ flow @ 530g/hr until
min 99 when set at 700
g/hr

minutes	Liquor Flow (gpm)	Air Flow (L/min) at STP	Cl ₂ outlet concentration (ppm)
0	1.8	25	0.1
3	1.8	25	0.1
7	1.8	25	0
15	1.8	25	0
21	1.8	25	0
28	1.8	25	0
31	1.8	25	0
34	1.8	25	0
39	1.8	25	0
48	1.8	25	0
54	1.8	25	0
58	1.8	25	0.1
64	0.6	25	0
67	0.6	25	0
69	0.6	25	0.1
80	0.4	25	0
82	0.4	46	
139	0.4	24	1
140	0.4	24	1.3
146	0.4	24	2.4
148	0.4	24	2.3
150	0.4	24	2.1
151	0.4	24	2
153	0.4	24	1.9
156	0.4	24	1.9
157	0.4	24	1.8

Table A.5: 0.1 M SO_3^{2-} Concentration Run

Air Flow const @ 24 L/min at
STP

Liquor Flow const @ 1.5 gpm

Cl_2 flow const @ 500g/hr

Time (min)	Cl_2 outlet conc (ppm)	total mol Cl_2 scrubbed	NaOH consumed (mol)
0	0.0	0	0
11	0.1		
12	0.2		
15	0.4		
32	0.4		
41	0.4		6.25
44	0.4		
47	0.4		
54	0.2	350	
57	0.2		
73	0.1		11.25
77	0.1		
82	0		
96	0		16.25
107	0		
112	0		18.75
114	0	740	

Appendix B

Sample Calculations

IC data to molarity for Cl⁻

Sample EQ-21-2 (second sample from 'half-sulfite run') gave a concentration of 770 mg/L for SO₃²⁻

Calculating concentration in terms of molarity:

$$770 \text{ mg/L} \times (1/1000) \times (1/80.605) = 0.03 \text{ mol/L}$$

Converting from concentration to total moles SO₃²⁻ in tank:

$$0.03 \text{ mol/L} \times 269 \text{ L} = 8.5 \text{ mol total}$$

Gas Flowrate Analysis using Ideal gas

These calculations were done for the mean and median values and presented in table 4.6

The air rotameter reading was converted to L through use of regression from calibration data:

$$1.9 \text{ (rotameter reading)} \times 12.8 \text{ (from calibration curve)} = 24 \text{ L/min}$$

This value was converted to moles using ideal gas:

$$(24 \text{ L/min} \times 101.325 \text{ kPa}) / (8.314 \text{ J/mol K} \times 298 \text{ K}) = 0.995 \text{ mol/min}$$

Mean Cl₂ concentration reading for the data was 6.6 ppm

Table A.6: Calculating the Gas Flowrate Analysis

Air Flowrate (rotameter)	Air Flowrate liters/min	Air flowrate (mol/min)	Cl ₂ outlet conc in ppm (avg)	Cl ₂ flowrate moles/min (average)
1.9	24	0.99	6.6	6.6 E-06

Calculating Scrubber Solution Capacity

Taking the average regression value for sulfite from Table 4.2:

$$\begin{aligned} \text{SSC} &= (\text{moles Cl}^-/\text{mole SO}_3^{2-}) = (1 \text{ mole Cl}_2 / 1.5 \text{ moles SO}_3^{2-}) \times (2 \text{ mole Cl}^- / \text{mole Cl}_2) \\ &= 1.3 \end{aligned}$$

Appendix C

Interpretation of Ion Chromatography Data

Ion Chromatography (IC) was used to monitor concentrations of sulfite (SO_3^{2-}), sulfate (SO_4), and chloride (Cl^-). Standard concentrations of solutions containing sulfite, sulfate, and chloride were made for each run to allow comparison of mobilities of these species in the experimental samples.

Spot checks were made where possible to assess the accuracy of the concentration readings of the IC data. Sulfite data corresponding to the beginning of experimental runs generally agreed well with the masses of sodium sulfite that had been weighed on a scale and added to the solution by hand prior to starting the run. For example, as mentioned in the discussion of Figure 4.1 in the experimental results section, the initial IC data point for the 'half sulfite' run provided a value 3% higher than the mass of sulfite as measured on the laboratory scale.

Chloride IC data was compared to data from the Cl_2 rotameter (flowrate) readings and also by weighing the Cl_2 cylinder before and after its use in an experimental run. The raw chloride IC data generally indicated concentrations lower than were the masses given by the rotameter readings and from the mass provided by weighing the Cl_2 cylinder. This is because the Chloride IC data gave results for Cl^- in solution, but not for OCl^-/HOCl which were the other species present in the liquid phase of the process in significant concentrations.

Weighing the cylinder directly was considered the most straightforward and reliable method of measuring mass of Cl_2 flowed to the process because both rotameter

readings and IC data both had to be calculated indirectly. Mass flowrates from rotameter data were calculated from the volumetric flowrates and ideal gas equation, and IC data meanwhile relied on the relative mobilities to allow the calculation of concentration. Although flowrates given by the rotameter readings were mostly in good agreement with the data from weighing the cylinder, a linear correction to the rotameter data was applied by scaling the data to the values provided by weighing the cylinder at the beginning and end of each experiment. This correction was made by assuming that the data point for total chlorine flowed through the process associated with the rotameter flowrates corresponding to the end of the run should be equivalent to the difference between the masses taken on the scale. As an example, Table C.1 shows the masses of the cylinder taken before and after the run made with a starting concentration of 0.025 M sulfite ‘half sulfite’ run.

Table A.7: Determination of total Cl₂ used for the no sulfite run

Initial Cylinder Mass (g)	Final Cylinder Mass (g)	Cl ₂ used (g)
6712	5640	1072

The data from table A.7 were then used to correct the rotameter data. The rest of the rotameter values were adjusted by assuming that the ratio of the last data point and the value in table A.7. This approach was appropriate because of the linear behavior observed in the calibration curve of the rotameter (F2). This approach is shown in table A.8

Table A.8: Linear correction applied for the Cl₂ flowrate data based upon the total mass of Cl₂ flowed as determined in Table A.7

Total Cl ₂ flowed (flowmeter) (g)	Total Cl ₂ flowed (flowmeter) (g) – corrected
0	0
283.2	225.43
561.52	446.97
762.18	606.69
916.95	729.89
1346.97	1072.19

The amount of OCl⁻ in the tank could then be estimated by taking the difference of the corrected Cl₂ flowed and the number of moles of Cl⁻ in the tank as determined from the chromatography data. This approach is valid because OCl⁻ is one of the dominant forms of chlorine present in the solution along with Cl⁻. HOCl was assumed to be negligible because of the high pH as shown in Figure 2.2. The calculation also assumes that desorption of HOCl is negligible. Calculation of OCl⁻ is shown in Table A.9.

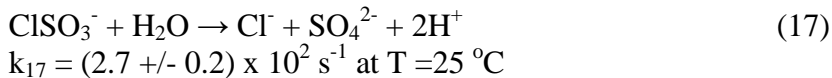
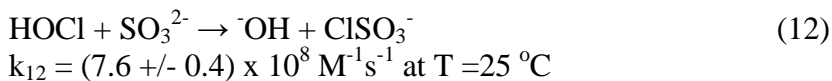
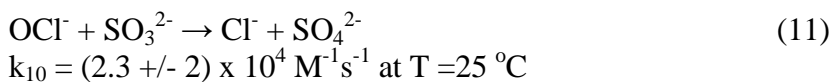
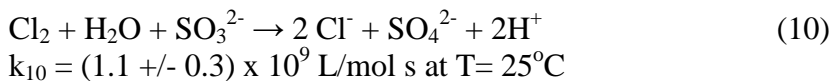
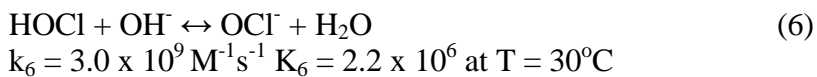
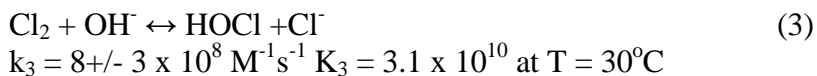
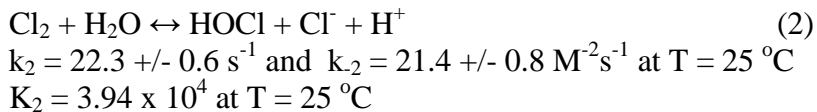
Table A.9: Estimate of moles of OCl⁻ in the scrubbing liquor tank; values obtained by subtracting the moles of Cl⁻ from the corrected Cl₂ data determined in Table A.8.

Total Cl ₂ flowed (rotameter) (mol) – corrected	Cl ⁻ IC data – total mol in tank	OCl ⁻ / HOCl total mol in tank
0	0	0
3.18	4.57	3.1
6.3	8.14	4.76
8.56	10.32	7.38
10.29	12.72	9.38
15.12	18.11	12.13

The data in Table A.9 was used to create Figure 4.9.

Appendix D

List of chemical reactions with equilibrium and rate constant data



Appendix E

List of Physical Constants and other Notable Information

Table A.10: Diffusivities of relevant species in water

Component	Diffusivity of Component in Water at 25°C $D_i \times 10^5$ (cm ² /s)	Reference
Cl ₂	1.96	Leaist, pg 1487
Cl ⁻	2.033	Leaist, pg 1487
Cl ⁻	2.072	Hikita et al., pg 77
HOCl	1.54	Hikita et al., pg 77
HOCl	1.49	Leaist, pg 1487
OCl ⁻	1.163	Hikita et al., pg 77
OH ⁻	3.434	Hikita et al., pg 77
H ⁺	9.315	Leaist, pg 1487

Characterization of Mass Transfer of Cl₂ scrubbing systems under different conditions

Adams (1937) studied Cl₂ absorption by aqueous NaOH.

10-20% by mole Cl₂ inlet flow

Limiting resistance was found to be liquid phase mass transfer.

Lahiri (1983) also studied Cl₂ absorption by aqueous NaOH.

50-64% by mole Cl₂ inlet flow

Limiting resistance was found to be liquid phase mass transfer.

Roy (2004) studied aqueous sulfite/bisulfate solution at pH 4.7 and 5.7.

Limiting resistance was found to be gas phase mass transfer when the condition $10 \cdot P_{Cl_2} <$

$[S(IV)]$ was applicable to the system, where P_{Cl_2} is partial pressure of Cl₂ in atm and

$[S(IV)]$ is combined concentration of SO₃²⁻ and HSO₃⁻ in mol/L

Solubility Data for Cl₂ in water

Extensive data can be found from Adams (1937).

Appendix F

Detailed Experimental Procedure and Equipment List

List of equipment labels in figures 2.1, 2.2, and 2.3 on pages 23, 24 and 25 respectively

T1 - Surge tank

R1 - opens N₂ flow to Cl₂ cabinet

R2 - regulates Cl₂ flow from cabinet to process

R3 - regulator for Cl₂ cylinder

S1 - actuator valve to open N₂ purge flow through V2

S2 - actuator valve to open solenoid valve V4

S3 - actuator valve to open solenoid valve V3

S4 - actuator valve to open solenoid valve V1

V1 - opens house air stream to Cl₂ cabinet and process air

V2 - opens Cl₂ in Cl₂ cabinet

V3 - opens Cl₂ flow from cabinet to R2 and overall process

V4 - opens Cl₂ cabinet safety vent

V5 - Surge tank release valve

F1 - Rotameter controlling Cl₂ flowrate to process

F2 - Rotameter controlling ambient air flowrate to process

F3 - Rotameter controlling scrubbing liquor flowrate to process

P1 - scrubbing liquor pump

P2 - Ultima MSA sampling diaphragm pump

A1 - Access point to T1 for pH probe

A2 - Access point adjacent to process gas inlet to T1

Detailed Experimental Procedure

1. The Cl₂ cylinder is weighed before operation and the mass is recorded. The cylinder is then placed back into the safety cabinet and securely reattached to its regulator R3.
2. Scrubber solution is prepared by adding appropriate mass of sodium sulfite (1.65 kg for 'standard case' concentration) to a convenient volume of water in a bucket. The mixture is stirred manually until solute is fully dissolved. Aqueous sulfite mixture is added to tank T1 through pH controller port/access port A1.
3. Tap water is then added through access port A1 until 265 L total solution is reached (when 8 ¼" below the top of A1).
4. The automatic pH controller is calibrated using a two-point calibration with buffers at pH 7.00 and 10.00. The pH controller is then checked with a standard buffer at pH 12.45.
5. The scrubber liquor pump P1 is turned on. Flowrate of scrubbing liquor can be controlled through rotameter F5.
6. Caustic pH control solution is mixed in a beaker with 2 L tap water and 200 g solid NaOH. The pH controller is then set to 12. The controller's connections are checked to ensure that they are secure, and the pump can now be turned on. The controller automatically pumps the required volume of caustic to bring the system pH to 12. The volume of caustic solution required to bring the tank's scrubbing solution to pH 12 is recorded. Fresh batches of caustic solution are mixed over the course of the experiment, and they are hooked up to the pH controller as soon as the previous batch is exhausted.

7. House air is turned on by turning on regulator R1, and the desired initial air flowrate for the experiment can be adjusted by rotameter F2.
8. The Cl₂ detector is switched on along with its sampling pump P2.
9. In anticipation of the Cl₂ being turned on, a final check is made that the system's access points are tightly closed and that the tubing conveying the main process stream is free of holes, and that the process is 'air tight.' This precaution ensures that the system is sealed and there is no chance of a Cl₂ leak. Leaks can be checked for by wafting ammonia around the process apparatus and tubing. If white smoke is seen, then Cl₂ is present. In the event of a Cl₂ related emergency or compromise in laboratory safety the valve S2 can be flipped to allow safe ventilation of the cabinet.
10. The Cl₂ is turned on by first carefully turning on R3, and then by opening S4 and finally opening valve S3.
11. Cl₂ flowrate is then adjusted to the desired level through F1. For 'standard conditions' the Cl₂ flowrate is set at 101 on F2.
12. A scrubber liquor sample is taken in a small container at valve V4 correspond to the beginning of the experiment (time = 0). Liquor samples are then taken to be processed by the ion chromatography system, preferably within one hour to avoid oxidation of the sulfite in the solution. Scrubber liquor samples continue to be taken regularly throughout the experiments. Samples were usually taken at a time corresponding either to the exhaustion of a 2L batch of caustic pH control solution or with changing of an experimental variable. The time at which the samples were pulled was always recorded.

13. Other process variables also are adjusted and noted in the laboratory notebook as the experiment progresses. Readings of variables such as Cl_2 , air, and liquor flowrates, Cl_2 effluent concentration, pH, scrubbing solution temperature, caustic consumption, and any other observations deemed relevant were recorded along with the corresponding times at which they were taken.

14. When the experiments have been run to the desired extent, the shutdown and cleanup procedure can begin. R3 is closed to shut down Cl_2 . Valve S1 is opened to allow a N_2 purge to clear the tubing in the cabinet of Cl_2 . N_2 remains on for at least 1 minute to allow for a thorough purge. S2, S3, and S4 are all opened and closed during this time to allow N_2 to freely flow throughout the tubing in the cabinet.

15. The pH controller can be turned off or set to feed no caustic.

16. The scrubbing solution is drained from the tank T1 at valve V4.

17. After the tank is emptied of scrubbing liquor the tank is rinsed and partially filled with tap water again through port A1. This step allows the system to be rinsed of residual chemicals to prevent corrosion and prepare for the next experimental run. The tap water is now emptied from the tank, again at V5.

18. The pump P1 can be turned off, as can the Cl_2 detector and its pump.

19. The pH controller electrode is detached from A1 and is stored in de-ionized water to allow for consistent performance.

20. The Cl_2 cylinder is again carefully and safely detached from the cabinet and is again weighed on a scale with the final mass being recorded. The Cl_2 cylinder is then returned to the safety cabinet in the next experiment.

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