

THE EFFECT OF pH ON HYDROGEN SULFIDE AND CARBON DIOXIDE ABSORPTION IN PACKED TOWERS

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ABSTRACT

Packed tower wet scrubbers have been the work-horse technology for hydrogen sulfide removal in the odor control industry for over 20 years. They typically operate at high pH through addition of an alkali such as sodium hydroxide, and with an oxidant such as chlorine added as sodium hypochlorite. Wet scrubbers provide high levels of hydrogen sulfide removal when operated at their designated design and operating parameters.

Carbon dioxide is a natural component of the ambient air. It is also a by-product of microbial respiration. Therefore it is present in the headspace of sewers and covered wastewater treatment processes where biological activity may be occurring, and where the gases from this activity may be released, such as from the headworks of wastewater treatment plants, aerated grit chambers, primary clarifiers and aeration tanks. Like hydrogen sulfide, carbon dioxide is an acid gas and is absorbed in alkaline conditions. As a result its absorption adds to the alkali demand and operating cost of wet scrubbers.

This paper presents the results of an optimization study of a wet scrubber odor control system that evaluated hydrogen sulfide and carbon dioxide removal, operating pH and chemical usage. Hydrogen sulfide and carbon dioxide removal were monitored at varying operating pH levels using continuous gas phase analyzers with data logging capabilities.

This paper provides important insight into potential cost saving operating strategies for owners and operators of wet scrubber systems.

KEYWORDS

Packed tower wet scrubbers, hydrogen sulfide absorption, carbon dioxide absorption, sodium hydroxide, sodium hypochlorite

INTRODUCTION

A packed tower wet scrubber system that uses sodium hydroxide and sodium hypochlorite was experiencing greater than expected sodium hydroxide usage. The packed tower wet scrubber system is used to control odor emissions at a wastewater treatment plant from the covered headworks and aeration tanks. It is a two-stage system with the packed tower wet scrubbers serving as the first-stage, and carbon adsorbers the second-stage. In response to the high sodium hydroxide usage, a field study was conducted to evaluate performance and optimize chemical usage. The inlet and exhaust of the wet scrubbers were analyzed for hydrogen sulfide and carbon dioxide using continuous monitors while the scrubbers were

operated over a pH range from 9.0 to 10.5. Hydrogen sulfide and carbon dioxide removal efficiencies were determined.

MATERIAL AND METHODS

System Description

The sources of odorous air treated by the subject odor control system are:

- Headworks (influent channel, bar screen room), degritting room and scum concentration room – 215,000 cfm
- Aeration Tanks – 79,000 cfm
- Total = 294,000 cfm

The subject odor control system is a two-stage system with packed tower wet scrubbers serving as the first-stage, and carbon adsorbers the second-stage.

There are eight packed tower wet scrubbers each with a capacity of 49,000-cfm which are configured to operate in parallel. Six operate to treat the design air flow rate of 294,000-cfm with the remaining two in standby mode. All eight scrubbers receive their inlet air from a common air plenum. There is a fan on the downstream side of each wet scrubber. The scrubber fans pull air through the scrubbers and discharge to a plenum. The carbon adsorber fans pull air from the scrubber discharge plenum. Table 1 is a design summary for the packed tower wet scrubbers. The scrubbers had a target makeup rate of 10-gpm, and were also equipped with an automated rapid fill line which was activated when the liquid level in the sump dropped below a set-point.

Table 1. Packed Tower Wet Scrubber Design Summary

Parameter	Value
Quantity	8
Air Flow Rate each, cfm	49,000
Diameter, ft	11
Packing Depth, ft	10
Packing Size, Type	3.5-inch Jaeger Tri-Packs
Recirculation Rate, gpm	980
Sodium Hydroxide Feed Pump Capacity, gph	3.0
Sodium Hypochlorite Feed Pump Capacity, gph	16
Target Blowdown Rate, gpm	10

The scrubbers employ traditional alkaline-oxidant chemistry for hydrogen sulfide (H₂S) removal. The alkaline condition shifts Equation 1 to the right, so that a non-volatile, ionized form of sulfide shown as sodium sulfide (Na₂S) predominates, significantly enhancing the driving force for hydrogen sulfide absorption above what that would be present if water at a neutral pH were used.



Chlorine is added to oxidize the absorbed hydrogen sulfide according to Equation 2 which further enhances the driving force for hydrogen sulfide absorption by eliminating any soluble ionized sulfide from the scrubbant, and providing additional driving force for Equation 1 to proceed to the right.



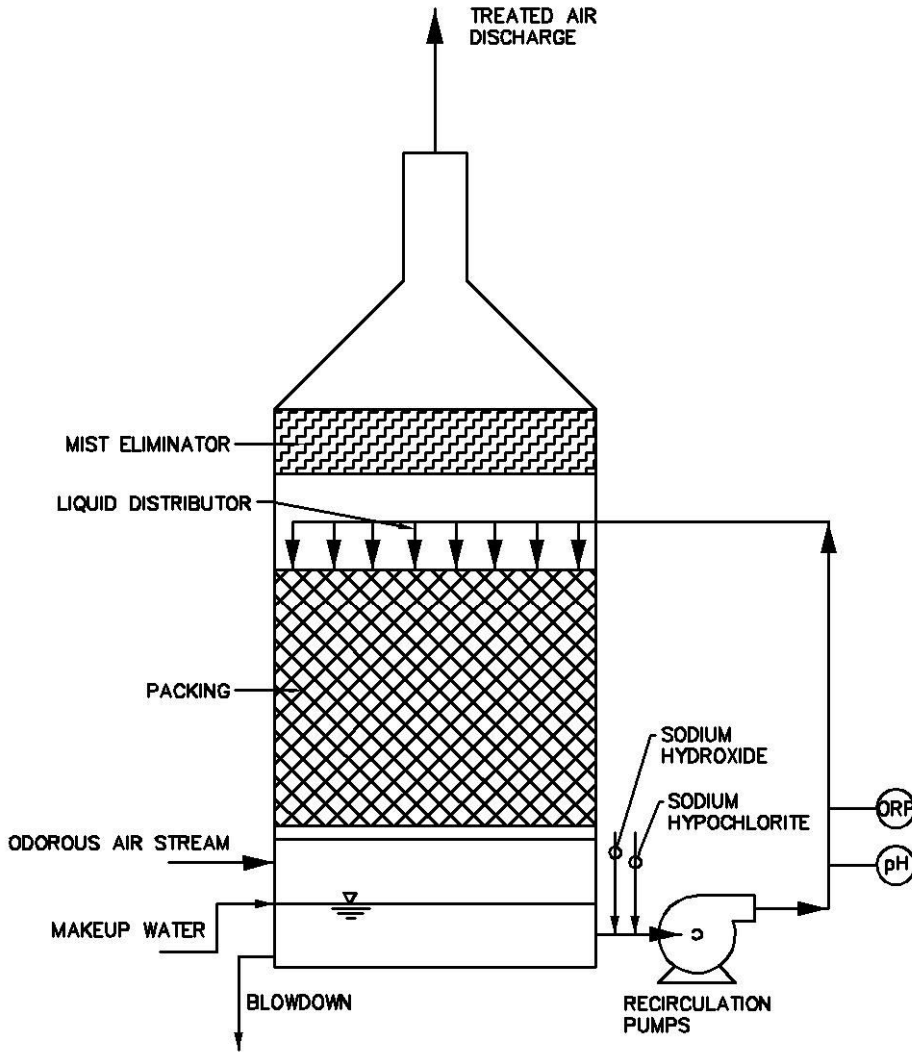
Makeup water is added to the scrubber on a continuous basis to replenish water lost through evaporation and carryover (water droplets/moisture entrained in the scrubber exhaust air stream), and to displace a portion of the scrubbant to drain. The displaced scrubbant solution is referred to as blowdown. The purpose of the blowdown in the subject scrubber system is to remove dissolved salts which over time may limit the absorption of hydrogen sulfide and to prevent salt buildup on the packing. In other scrubber systems the blowdown serves as the mechanism to remove absorbed constituents from the scrubbant, thereby maintaining a gradient between the actual and equilibrium gas phase concentration in the scrubbant to ensure continuous absorption. As noted above for the subject scrubbers, this driving force is achieved through chemical oxidation of the absorbed hydrogen sulfide. However, as will be discussed below, the blowdown of the subject scrubbers helps provide a driving force for carbon dioxide absorption.

The addition of 25% sodium hydroxide is controlled by a pH control loop. Chlorine is added as sodium hypochlorite and its addition is controlled by an oxidation-reduction-potential (ORP) control loop.

The second stage of the system consists of 22 carbon adsorbers. The size of the carbon adsorbers varies. The number of carbon adsorbers online is consistent with the number of operating wet scrubbers.

Figure 1 is a schematic of the packed tower wet scrubbers in this odor control system.

Figure 1. Typical Schematic of Packed Tower Wet Scrubber



**FIGURE 1
PACKED TOWER WET SCRUBBER**

Analytical Methods

Hydrogen Sulfide. A Thermo Environmental Instruments (TEI) 450CTL unit was used to monitor for hydrogen sulfide (H₂S) in the inlet and exhaust of the scrubber selected for testing. The TEI 450CTL consists of a hydrogen sulfide-to-sulfur dioxide (SO₂) converter coupled to a pulsed fluorescence SO₂ analyzer. Air is pumped into the instrument for analysis. Continuous hydrogen sulfide monitoring is conducted by converting the hydrogen sulfide in the sample to sulfur dioxide according to the following reaction:



The converter section of the TEI 450CTL catalytically converts each hydrogen sulfide molecule to sulfur dioxide so that the output of the sulfur dioxide analyzer is equal to the concentration of hydrogen sulfide entering the converter. Any sulfur dioxide present in the original sample is scrubbed prior to its entrance into the converter, providing an instrument response that is hydrogen sulfide specific. A sample averaging time of 10 seconds was used which provided a detection limit of 1.0-part per billion by volume (ppbv).

A sequencer was used with the TEI 450CTL unit which enables up to five locations to be sampled sequentially by a single TEI 450CTL unit. The sequencer was used to monitor the inlet and exhaust hydrogen sulfide concentrations. Given the time required to purge the instrument between samples, an analysis was recorded every three minutes. Teflon® tubing was used to convey samples from the test scrubber inlet and exhaust to the sequencer. Filters were installed on the ends of the sample lines to protect the sequencer and TEI 450CTL from particulate matter.

The TEI 450CTL has an RS-232 interface that was used to download data to a computer using TEI's communications software.

Carbon Dioxide. The scrubber inlet and exhaust carbon dioxide concentrations were measured using two TEI 41 CHL (high level) monitors. One unit was used for the scrubber inlet and one for the exhaust. The TEI 41 CHL has a measurement range of 0 – 2,000 ppm. It uses an infrared detector and the absorption of infrared radiation by carbon dioxide as a basis for the measurement of this gas. Teflon tubing conveyed air from the test scrubber inlet and exhaust to the respective monitors. Carbon dioxide calibration gas (1,000-ppm_v) was used to calibrate both units daily.

This unit also has an RS-232 interface which enabled the downloading of data using the same communications software that was used for the TEI 450CTL unit.

Scrubbant Solution Measurements

Measurements were made of the blowdown from the scrubber to obtain snapshots of the chemical conditions affecting hydrogen sulfide absorption (dissolved sulfide, chlorine residual, pH and ORP).

Dissolved Sulfide. Sulfide is present in solution as hydrogen sulfide (H₂S), a dissolved gas, and as dissolved ions: hydrosulfide (HS⁻) and sulfide (S⁻²). The percentage of each species in solution is pH dependent. At pH 7.0 there is approximately 50% hydrogen sulfide and hydrosulfide present. Total dissolved sulfide in the scrubbant solution was measured using a LaMotte Sulfide Test Kit, Model CC-PS. This test kit uses the Methylene Blue method for sulfide measurement and has a detection limit of 0.1 mg/l. Total sulfide measures all sulfide present in the sample (i.e., hydrogen sulfide, hydrosulfide and sulfide).

Chlorine Residual. Chlorine can be found in solution as either hypochlorous acid (HOCl) or hypochlorite ion (OCl⁻). At a pH of 7.3 there are approximately equal concentrations of both the hypochlorous acid and the hypochlorite ion. The hypochlorite ion dominates at pH values greater than 7.3 while the hypochlorous acid molecule is a more potent oxidizer.

Free chlorine, or the chlorine residual that is still active to oxidize, includes hypochlorous acid and the hypochlorite ion. When free chlorine is measured, it includes both species. At high levels, the free chlorine was measured using a Hach Test Kit Model CN-21P. This test kit has a range of 10-200 mg/L. For measurement of low levels of free chlorine a Hach Test Kit Model CN-80 with a range of 0-10 mg/L was used.

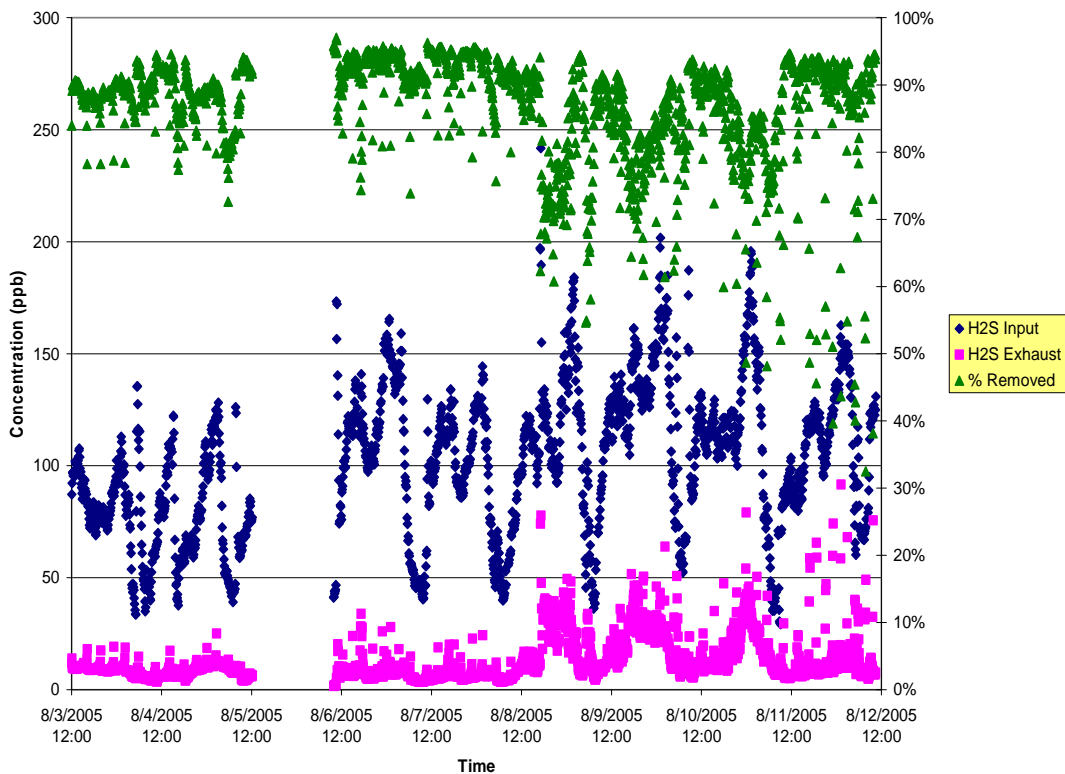
pH and ORP. pH and ORP measurements were obtained from the packed tower wet scrubber monitoring system.

RESULTS AND DISCUSSION

Hydrogen Sulfide. The inlet hydrogen sulfide concentrations ranged from approximately 20 ppbv to 200 ppbv, with a median inlet concentration of 105 ppbv. Inlet, exhaust and percent removal is shown in Figure 2, with a percent removal range of approximately 40% to 97% removal over the pH range of 9.0 to 10.5.

Dissolved sulfide measurements in the scrubbant were less than 0.1-mg/l, the detection limit for the LaMotte kit. The chlorine in the blowdown ranged from 5 to 30-mg/l. The ORP was maintained above 500-mV.

Figure 2. H₂S Inlet, Exhaust, Percent Removal



Percent removal and operating pH is shown in Figure 3 which shows percent removal generally above 90% at pH values of 10.0 and greater, and a small decline in percent removal at pH values less than 10.0.

Figure 3. H₂S Percent Removal vs pH

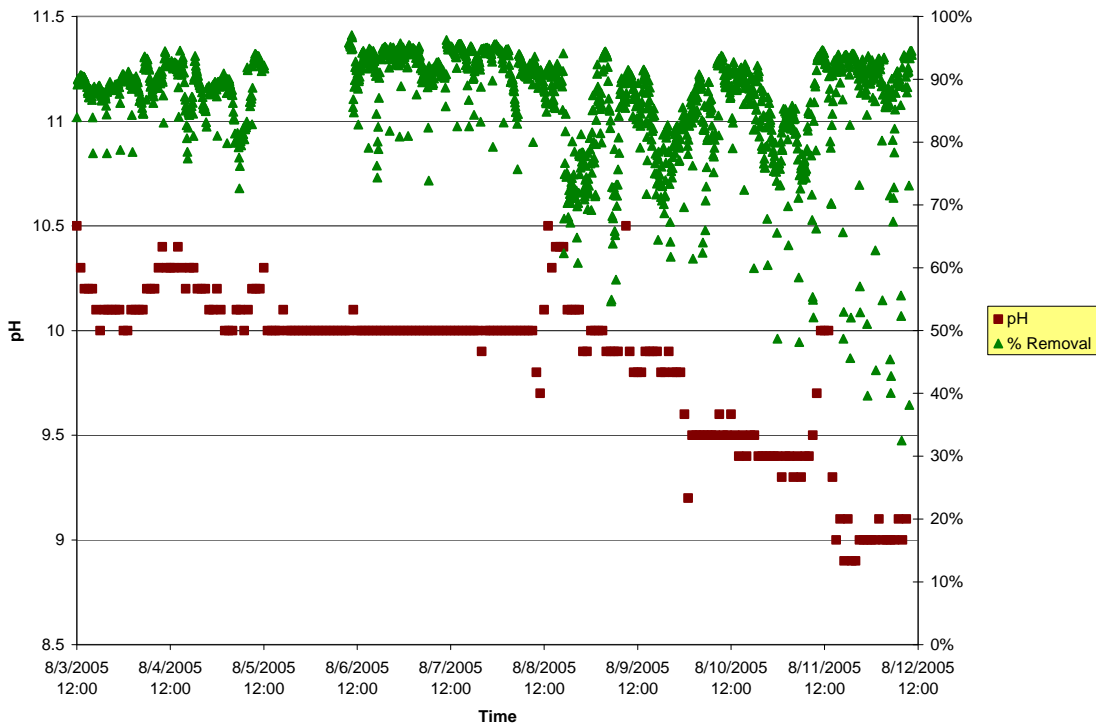


Figure 4 shows the theoretical speciation of hydrogen sulfide, hydrosulfide and sulfide as a function of pH. At a pH < 4, a very low concentration of hydrogen sulfide is present in solution. At increasing pH values from 4.0 to 10, the fraction of hydrogen sulfide decreases and hydrosulfide increases. At pH values > 10 the fraction of hydrogen sulfide present is low, whereas the fraction of hydrosulfide is > 99% of the total sulfide species present. Operating at a higher pH increases the absorption rate by reducing any back-pressure of hydrogen sulfide in solution and increases the overall percent removal of the column. With an oxidant present in solution, in this case chlorine, any dissolved sulfide in solution is quickly oxidized, and the impact of pH as long as it is greater than 9.3 is not significant.

Figure 5 is a frequency distribution for the measured percent removal of hydrogen sulfide at different pH values. The data shows minimal variation at the 50% frequency occurrence, with the percent removal for pH values of 10.5, 10.0 and 9.0 ranging from 89 to 92%. The removal efficiency at pH 9.5 was 84% at the 50% frequency interval which is discounted due to potentially erroneous exhaust hydrogen sulfide readings.

It is noted that hydrogen sulfide was removed at 99 percent efficiency by the columns tested in this study during their startup with the inlet augmented to a concentration of 5-ppm_v. For startup, the inlet concentration was measured with an Interscan device and the exhaust by a Jerome meter. It is suspected that a lower driving force at a lower inlet concentration may cause reduced removal efficiencies.

Figure 4. Speciation of H₂S at Different pH Values

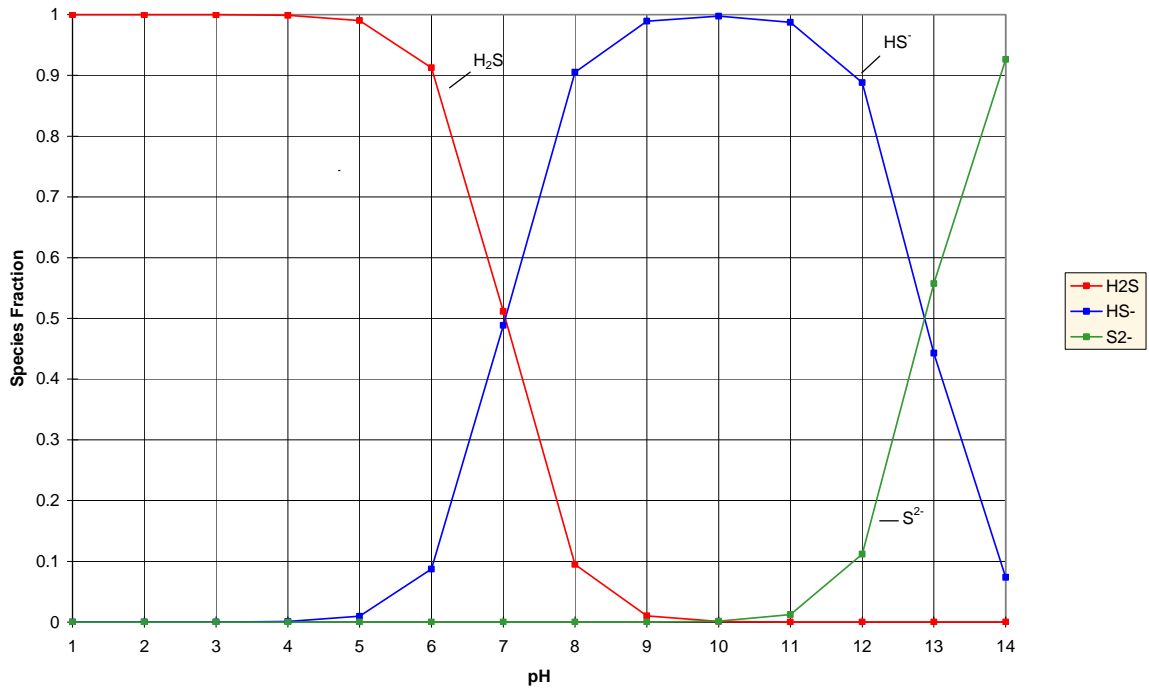
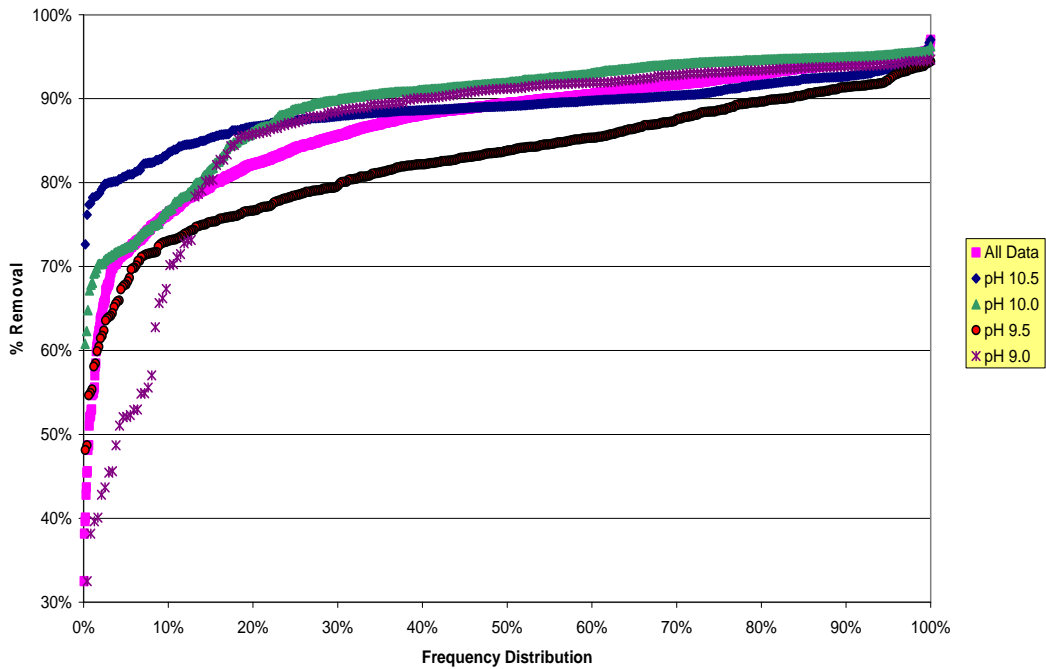


Figure 5. H₂S Percent Removal Frequency Distribution



Carbon Dioxide

Carbon dioxide is present in solution in three forms: carbonic acid (H₂CO₃), bicarbonate (HCO₃⁻) and carbonate (CO₃⁻²) as shown in Equations 4 to 6. At increasing pH, the carbonate species present and their respective fractions shift from carbonic acid (H₂CO₃), to bicarbonate (HCO₃⁻), to carbonate (CO₃⁻²).

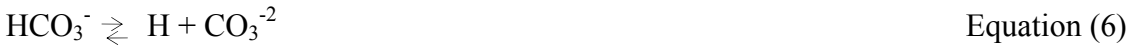
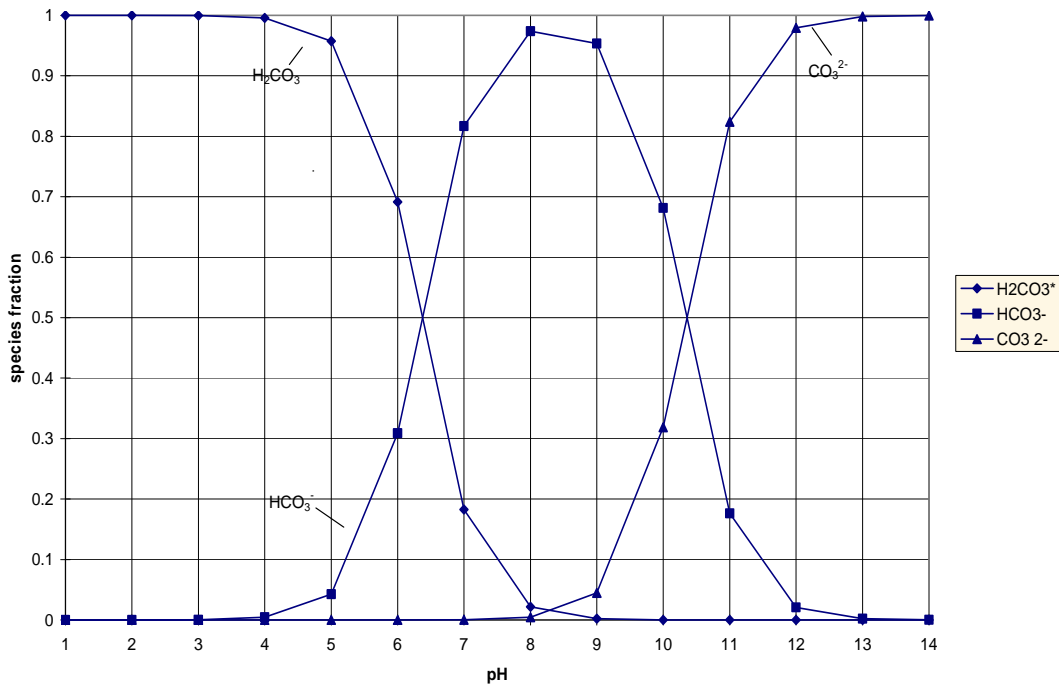


Figure 6 shows the distribution of these species graphically as a function of pH.

Figure 6. Speciation of the Carbonate System at Different pH Values



As pH increases, the presence of carbon dioxide in solution decreases and its partial pressure above the solution decreases which increases the driving force for its absorption. Conversely, as pH decreases, the fraction of carbon dioxide in solution increases and the driving force for absorption is reduced. The fraction of carbon dioxide present relative to the total carbonate species as a affect of pH can be expressed by manipulating the carbonate system equilibrium equations.¹ Equation 7 expresses the unionized fraction of a diprotic acid, carbon dioxide in this case.

$$A_o = 1/(1 + K_1/[H^+] + K_1 K_2/[H^+]^2) \quad \text{Equation (7)}$$

K1 = first ionization constant
 K2 = second ionization constant
 [H⁺] = hydrogen ion molar concentration

For packed tower design and performance evaluation purposes, the ionized fraction can be used to modify the Henry's Law Coefficient as shown in Equation 8. This concept has been introduced previously in the literature.²

$$H' = y/xA_o \tag{Equation (8)}$$

Where,

H' = Adjusted Henry's Law Coefficient, atmosphere/mole fraction
 y = partial pressure of the gas, atmospheres
 x = concentration of gas in solution, mole fraction

The inlet carbon dioxide concentration ranged from 1,175 to 1,800-ppm_v, with a median value of 1,475-ppm_v. The average percent removal of carbon dioxide ranged from approximately 9.2 to 1.5% over the operating pH range of 10.5 to 9.0. Figure 7 is a graph of inlet, exhaust concentration and percent removal.

Figure 7. Carbon Dioxide Inlet, Exhaust, Percent Removal

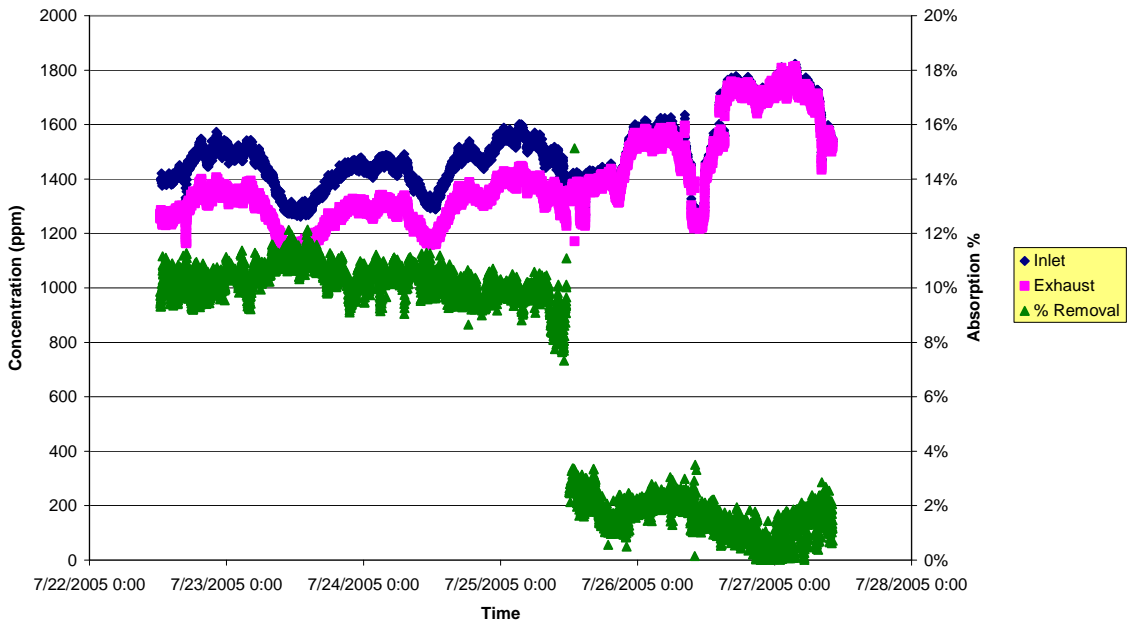
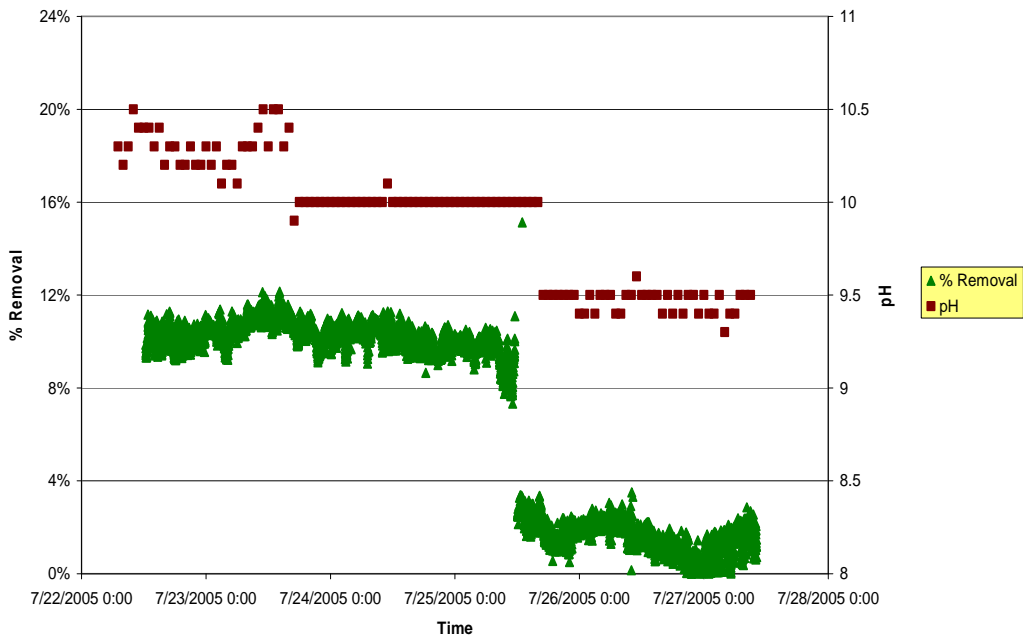


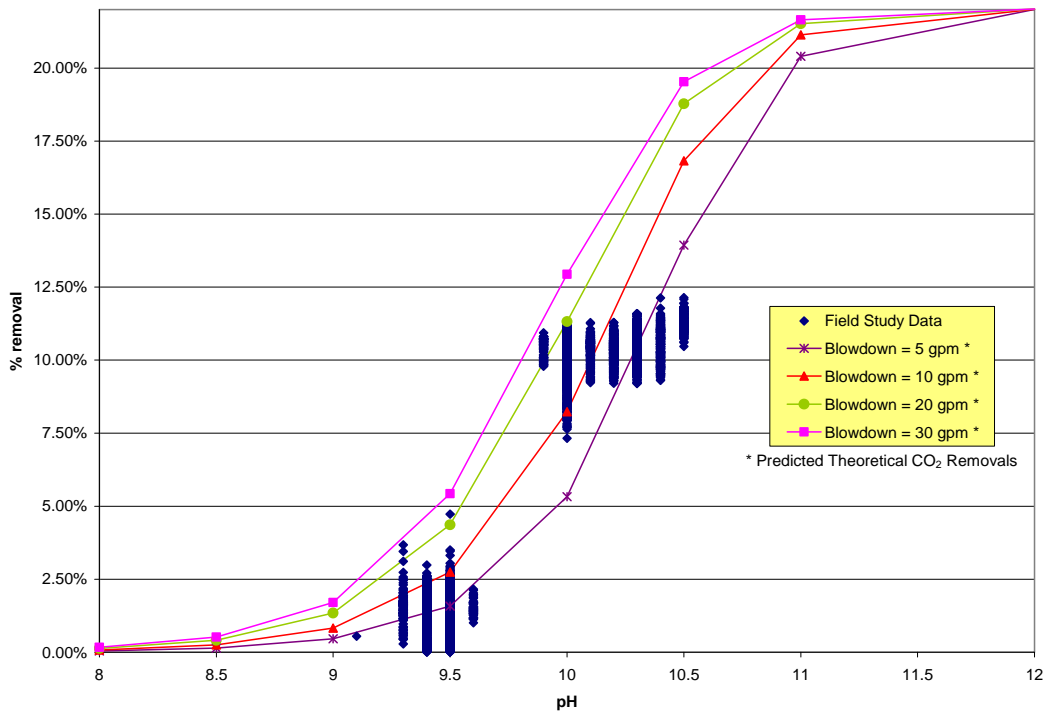
Figure 8 is a graph of carbon dioxide percent removal vs pH. The graph shows a removal efficiency of 8 to 12% at pH values ranging from 10 to 10.5, and of less 1 to 3.5% at pH values ranging 9.3 to 9.5.

Figure 8. Carbon Dioxide Percent Removal vs pH



Using an adjusted Henry’s Law Coefficient for carbon dioxide, mass balance calculations around the scrubber, a carbon dioxide mass transfer coefficient, and the operating parameters for the subject packed tower wet scrubber, predicted carbon dioxide removals were determined as a function of pH and blowdown rate. The predicted and the observed field study carbon dioxide removals are presented in Figure 9 which show agreement over a blowdown range of approximately 5 to 30 gpm. While the target makeup rate was 10-gpm it is suspected that higher blowdown rates may have occurred when the rapid fill to the scrubber was activated. Lower blowdown rates may have resulted from a variation in the rotameter setting.

Figure 9. Observed and Predicted Carbon Dioxide Removal as a Function of pH and Blowdown Rate



Sodium Hydroxide Usage

At the inlet hydrogen sulfide and carbon dioxide concentrations for this odor control system, sodium hydroxide usage was primarily for carbon dioxide absorption which provides no odor control benefit. As a result, it was recommended that the operating pH be reduced to 9.5 or less. At pH 9.5 it was estimated sodium hydroxide usage would be reduced from approximately 4,000 to 600 lbs/day.

CONCLUSIONS

The following conclusions are made given the inlet hydrogen sulfide and carbon dioxide concentrations of the subject odor control system:

- Operating within a pH range of 9.0 to 10.5 with sodium hypochlorite had limited effect on hydrogen sulfide removal efficiency.
- Operating at a lower pH reduced carbon dioxide absorption from approximately 10% at pH 10, to 1.5% at pH 9.5.
- By operating at pH 9.5, it was estimated that sodium hydroxide usage would be reduced from approximately 4,000 to 600 lbs per day for an annual savings of \$310,000.

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