

Application of Packed Scrubbers for Air Emissions Control in Municipal Wastewater Treatment Plants

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The process air emissions from municipal wastewater treatment plants primarily consist of hydrogen sulfide gas, along with other organo-sulfur compounds, and some trace quantities of volatile organic compounds (VOC). Various Federal and/or State Regulations require monitoring, and control of these emissions down to some specified levels.

At the Deer Island Wastewater Treatment Plant of the Massachusetts Water Resources Authority (MWRA), air containing hydrogen sulfide is collected and treated in several emission control systems. These systems consist of wet scrubbers which facilitate destruction of hydrogen sulfide gas and the related odor by continuously contacting the collected air counter-currently with a strong oxidizing solution of sodium hypochlorite.

This paper reviews the performance of a typical scrubber in light of the theory of absorption followed by chemical reaction. Based on an analysis of a set of test data, it has been concluded that when the concentration of hydrogen sulfide at a scrubber inlet exceeds 25 ppm, the scrubber becomes mass transfer limited. This can lead to the incomplete oxidation of hydrogen sulfide gas. Unreacted H_2S eventually can exit the scrubber while partially oxidized H_2S , in the form of elemental sulfur, can deposit on, and eventually foul, the packing media. Measures taken to overcome such a situation have also been reported.

INTRODUCTION

The Deer Island Treatment Plant of the Massachusetts Water Resources Authority (MWRA) is currently undergoing a major construction project. A secondary wastewater treatment facility is being built that will be coupled with the recently completed primary treatment phase. The

full build-out facility, projected for completion in 1999, will be able to meet U.S. Clean Water Act of 1992 (Public Law 92-500) effluent standards for up to 1.2 billion gallons of sewage per day.

One of the fundamental design criteria for the new treatment facility was to minimize deleterious effects of process vapors (from a regulatory standpoint, stack emissions of total reduced sulfides- TRS will probably be capped at 1 ppm). As such, all off-gas generation areas are enclosed, and the gases treated prior to stack emission. Off-gas treatment may include sulfide oxidation using sodium hypochlorite, ammonia removal using sulfuric acid, and volatile organic carbon (VOC) adsorption using activated carbon. Four of the eventual five unique off-gas treatment facilities are presently on line.

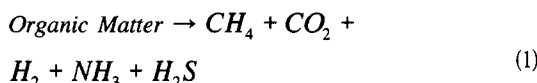
Hydrogen sulfide is the most common odorous sulfur compound found in municipal wastewater. If discharged untreated, hydrogen sulfide poses health and nuisance problems for plant workers and people in the neighboring community of Winthrop. It is also highly corrosive and will attack plant structures and equipment, resulting in costly repairs. Recent monitoring results indicate a summertime high of around 200 ppm of hydrogen sulfide in Deer Island process off-gases.

This paper reviews the chemistry and biology of the formation of hydrogen sulfide. The treatment kinetics are also examined. In addition, an overview is presented regarding the Deer Island treatment scheme and process performance with respect to hydrogen sulfide removal.

Vapor Phase Pollutants From Raw Municipal Sewage

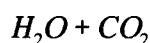
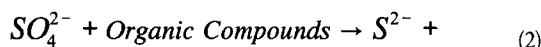
Human wastes contain sulfur in both organic and inorganic forms. Domestic wastewater contains significant amounts of sulfates, mainly from oxidized food wastes. Sulfates from surface water supplies and, in the case of coastal cities like Boston, sea water intrusion also contribute to the sulfate loading. The Deer Island wastewater treatment plant handles influent sulfate concentrations in the area of 80 to 100 mg/L. Household wastewater may

travel in excess of 30 miles, and take more than a day, to reach Deer Island for treatment. During that time, any free oxygen in the wastewater is quickly depleted by aerobic bacteria. Facultative aerobes and anaerobes dominate for the remainder of the trip, and cause the complex organic molecules in oxygen-depleted wastewater to undergo decomposition into breakdown products. The simplified overall reaction to gases is stated in Equation (1).



Methane production within the collection and wastewater treatment processes can lead to hazardous conditions, and is closely monitored. On the other hand, methane production is encouraged in the anaerobic sludge digestion treatment process, whereby it can be used as a plant energy supplement for heat or power generation. Ammonia gas may be present in sufficient quantities to influence odor levels, and as explained later, can be chemically reacted to salt. Hydrogen sulfide is the most common of the sulfur gases generated, and is typically the gas monitored in the control of odors. Other, less abundant sulfur containing volatile compounds such as mercaptans, however, are responsible for some of the strongest odors.

Sulfate reducing bacteria participate in the decomposition, and produce sulfides, mainly on the slime formations on walls of wastewater collection network pipes and eventual process equipment. The major pathway for hydrogen sulfide production by anaerobic bacteria is represented in Equations (2) and (3) [1].



Bacteria, such as the *Desulfovibrio desulfuricans*, can reduce sulfate to sulfide using fermented carbon sources as electron donors [1].

Important Physical and Chemical Properties of Hydrogen Sulfide

Hydrogen sulfide is a toxic, colorless, flammable gas that is heavier than air. It can accumulate in poorly ventilated areas such as manholes and other confined spaces, and become a safety risk. The odor threshold of hydrogen sulfide is about 0.00047 ppmv. The characteristic smell is that of rotten eggs, but rapid desensitization can occur, resulting in a false sense of safety. Hydrogen sulfide is toxic at higher concentrations and will cause rapid death at levels of 0.2%. In aqueous solution hydrogen sulfide dissociates according to Equations (4) and (5).



The distribution of species is pH dependent, as shown in Figure 1. Domestic wastewater pH is usually below 7 so that the fraction of sulfide as H_2S is typically above 0.5. Molecular hydrogen sulfide is fairly soluble in wastewater (3.6 g/L @ 20°C, 1 atm.). The vapor pressure of hydrogen sulfide in equilibrium between the aqueous and gaseous phases can be expressed by Henry's Law. The value of Henry's Law Constant for the water-hydrogen sulfide system at 25°C is $H_{A(\text{H}_2\text{S}@25^\circ\text{C})} = 54,500 \text{ atm/mol. fraction}$ [2]. Since the partial pressure is temperature dependent, gas release will be temperature dependent. Bacterial activity also increases at warmer temperatures, so that hydrogen sulfide gas generation and release to atmosphere will increase during the warmer months of the year. The turbulence of wastewater during the transport and treatment processes facilitates the release of gas.

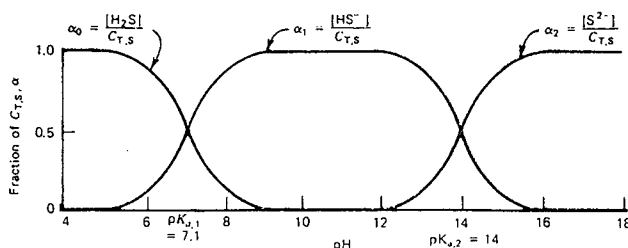


FIGURE 1. Distribution Diagram for H_2S [3].

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The Odor Control System Description at Deer Island

As previously mentioned, there are five (at full build-out) separate odor control systems on Deer Island. In reality, these five systems are considered as air pollution control facilities as smog contributors such as volatile organic compounds are also treated and controlled. All of the wastewater treatment processes are carried out in closed, continuously ventilated tanks and equipment (except for secondary clarification, which occurs in open tanks). Exhaust air from individual process headspaces of a given area is collected in a manifold and routed to the respective area air pollution control system. The odor control treatment processes adopted for a given area are based upon the type of gases present in the area equipment headspaces. The three air pollution control systems that are dedicated to pump stations and primary treatment are mainly concerned with hydrogen sulfide, some amounts of reduced organic sulfur compounds (e.g. mercaptans), and VOCs. In the area where anaerobic sludge thickeners are located, air is also expected to contain some amounts of ammonia and provisions for its scrubbing have been added. The biological secondary treatment process is aerobic, and conducted in the presence of pure oxygen. Therefore, secondary process emissions are not expected to contain any reduced inorganic compounds, e.g. hydrogen sulfide and ammonia, although there may be some amounts of VOCs which may be stripped from the wastewater during the treatment process. Since the wet scrubbing system for reduced sulfur compounds is the focus for this paper, air pollution control systems will be referred to as odor control systems.

The purpose of primary treatment is to remove wastewater pollutants by the physical process of sedimentation. Two independent odor control systems (designated East and West) serve the primary treatment areas at the plant. Each two-stage system is comprised of scrubbing towers followed by activated carbon beds. The counterflow, packed scrubbers remove sulfur containing compounds such as hydrogen sulfide, as well as some reduced organic compounds, from the air stream by oxidizing them with the help of an aqueous solution of sodium hypochlorite and sodium hydroxide. Any remaining VOCs may be removed by the activated carbon beds. Fans and fiberglass ducts facilitate collection and movement of air through the system.

Odorous air enters a scrubber tower from the bottom and travels upward through void spaces within a bed of 3.5" size polyethylene packing material. The scrubbing solution is sprayed from the top of the tower and flows down through the plastic media. This countercurrent motion between the gas and liquid phases creates turbulence and enhances the surface area of contact necessary for the control reaction. Under the prevailing conditions in the scrubber, the chemical reactions, as shown later, convert hydrogen sulfide to sodium sulfate, and sodium hypochlorite to sodium chloride. The liquid phase, traveling down the scrubber, carries these two products and collects in a sump at the bottom. The treated gas stream leaves the tower at the top, after moving through a mist eliminator, and enters (or bypasses, depending upon VOC concentration) the carbon adsorbers. Emissions are from tall exterior stacks.

Scrubber sump liquid is continuously recirculated to the top of the scrubber for reuse. When the aqueous solubility of any of the two product salts is exceeded, it appears in the liquid phase as fine, white solids. The solubility product of sodium sulfate ($K_{sp} = 10.29 @ 20^\circ\text{C}$) is much lower than that of

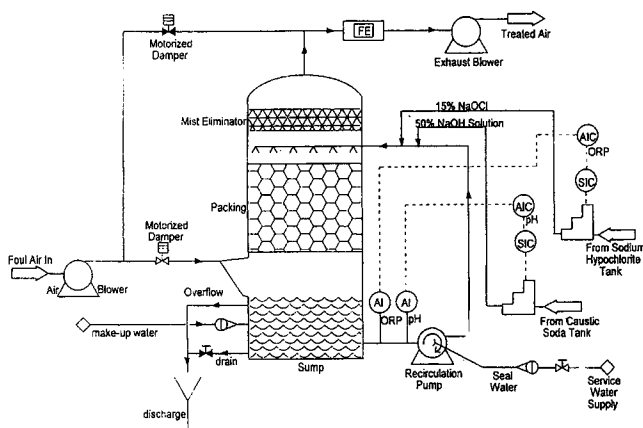


FIGURE 2. Diagram of scrubber.

sodium chloride ($K_{sp} = 37.72$ @ 20°C). The ionic product of sodium and sulfate ions (resulting from reaction) in the liquid system typically exceeds the solubility product of sodium sulfate, leading to the appearance of sodium sulfate particles. Most of these particles move out of the packing as suspended solids within the scrubbing solution, however some deposits may remain on the packing material. A measured amount (5%) of the scrubbing solution is continuously purged from the scrubber sump in the form of overflow. Failure to remove solids will eventually result in blockage within the media. Fresh make-up chemicals and water are continuously added to maintain liquid flow and oxidizing chemical concentration. A head loss monitoring system on the outside of the scrubber determines media solids buildup. Once the pressure drop reaches twice the original, the scrubber cycle is terminated and the medium is cleaned by recirculating a 3% muriatic acid (dilute HCl) solution over the packing for approximately 2-3 hours. Each of the odor control systems in the primary treatment area includes several parallel scrubbers. Within a particular odor control system, different scrubbers handle air from different primary areas. The concentrations of odorous gases handled by these scrubbers can therefore be different. Scrubbers that treat air from the headspace of the primary clarifiers handle the plant's maximum concentrations of hydrogen sulfide. Each primary odor scrubber has a handling capacity of 52,000 cfm, a diameter of $10^{\circ}-0^{\circ}$, and a packing depth of $10^{\circ}-0^{\circ}$.

The sodium hydroxide (50% NaOH) feed rate is controlled by feedback from a pH probe in the scrubbing solution recirculation loop. The pH set point is currently maintained between 10 and 11. The sodium hypochlorite (15% NaOCl) feed rate is similarly controlled by an oxidation reduction potential (ORP) probe set at 450-550 mv. Chemical metering pumps have been upgraded to meet the higher than anticipated summertime sulfide levels. A simplified process flow diagram of a primary scrubber system is shown in Figure 2.

Typical Air Inlet Composition and Flow Rate

The Deer Island Treatment Plant is currently undergoing an emissions monitoring program, designed to demonstrate the effectiveness of the air pollution control devices installed on various wastewater derived air emissions sources, and to verify acceptable pollutant emission rates. The requirements of the program are to conduct testing of various air pollution control devices and to monitor air emission streams for total reduced sulfur (TRS), total non-methane hydrocarbons (NMHCs), hydrogen sulfide (H_2S), ammonia (NH_3) and targeted volatile organic compounds (VOCs). A trailer mounted continuous emissions monitoring system (CEMS) was installed on Scrubber #3 at the West Odor Control Facility in June, 1996, with monitoring continued through October, 1996. The program was conducted with the help of ENSR, an environmental consulting firm located in Acton, MA.

According to the available data, the inlet air of scrubber #3 contains primarily H_2S , along with other organo-sulfur compounds, and some trace

Table 1. Typical Air Inlet Compositions to Emission Control Scrubbers
(All Compounds *Except* Hydrogen Sulfide)

Target Compound		Avg. Inlet Conc.(ppb)
Volatile Organic Compounds		
Chloromethane	<	3.5
Bromomethane	<	1.3
Vinyl Chloride		12
Chloroethane	<	1.9
Methyl Chloride		12
Acetone	<	24
1,1 -Dichloroethene		3.1
1,1-Dichloroethane		3.6
Trans 1,2-Dichloroethene	<	1.2
1,2-Dichloroethane	<	1.2
Chloroform		25
2-Butanone	<	8.3
1,1,1 -Trichloroethane		17
Carbon Tetrachloride	<	0.78
Bromodichloromethane	<	2.2
Vinyl Acetate		73
1,2 -Dichloropropane	<	1.1
Cis-1,3 -Dichloropropane	<	1.1
Trichloroethene		82
Dibromochloromethane	<	0.58
Benzene		21
Trans-1,3-Dichloropropene	<	1
1,1,2-Trichloroethane	<	0.9
Bromoform	<	0.95
4-Methyl-2-Pentanone	<	6
2-Hexanone	<	2.4
1,1,2,2-Tetrachloroethane	<	0.72
Tetrachloroethene		66
Toulene		48
Chlorobenzene		2.5
Ethyl Benzene		13
Styrene	<	1.2
Total Xylenes		50
Reduced Sulfur Compounds		
Methyl Mercaptan		50
Carbon Disulfide	<	33
Dimethyl Sulfide	<	27
Dimethyl Disulfide	<	22

quantities of VOCs. Typical air inlet compositions (besides H_2S) tested in the third quarter of 1996 are shown in Table 1. An example of the daily variation of hydrogen sulfide concentration is shown separately in Table 2. Two tables are used because of the difference in the order of magnitude of concentrations between hydrogen sulfide and other compounds. The seasonal variation of H_2S levels at the inlet is in the range of from 0.1 ppm in winter (Jan. - April) to as high as 200 ppm in late summer and fall (Aug. - Oct.). The level of NMHC at the inlet was between 9 ppm and 25 ppm during the third quarter of 1996, with less apparent seasonal variation than with H_2S . The air flow rate into each scrubber is stabilized by automatic adjustment of the inlet damper opening. The air flow rate into West Odor Control Scrubber #3 is set at 33,000 SCFM, as shown in Table 2.

Table 2. Continuous Emissions Monitoring Data for Total Reduced Sulfur

Scrubber ID: West #3 Date: September 30, 1996

Location	West Odor Control			Unit ID: Scrubber #3
	Air	Inlet TRS	Outlet TRS	TRS Removal
Time	Flow Rate (scfm)	(ppm)	(ppm)	Efficiency %
13:00	32750	24.25	0.14	99.4
17:00	32750	41.16	0.04	99.9
18:00	32750	50.84	0.03	99.9
19:00	33000	55.84	0.03	99.9
22:00	33000	67.91	0.02	100
23:00	33000	64.83	0.02	100

Design Basis

The original process design and sizing of West Odor Control Scrubber #3 were based upon the following criteria:

- Air flow rate = 40,000 SCFM
- Inlet H₂S level = 5 ppm (v/v)
- Required removal efficiency of H₂S > 99%.

However, after monitoring for about a year, the actual summertime H₂S in the inlet air was observed to reach levels two orders of magnitude higher than the original estimate. This resulted in unacceptably high H₂S concentrations in the air released from the odor control system. To overcome this situation, larger capacity sodium hypochlorite and sodium hydroxide metering pumps have been installed, parallel to the original pump, to fulfill the summertime demands. Nothing else has been changed in the scrubber system,

Table 3. Raw Data and Calculated Results on Chlorine and Sulfur Species material Balance

Scrubber ID: West #3 Date: September 30, 1996

Time (Hour)	Air Phase H ₂ S		NaOCl Feeding			NaOH	Water
	Influent lb/hr.	Effluent lb/hr.	[OCl ⁻] mg/L	[Cl ⁻] mg/L	Flow gal/hr	Flow gal/hr	Flow gal/hr
13:00	4.51	0.03	99210	92640	31	15.75	300
17:00	7.66	0.01	96490	95360	9.35	12.39	300
18:00	9.46	0	95810	96040	35.24	10.47	300
19:00	10.47	0	95130	96720	28.89	13.79	300
22:00	12.73	0	93090	98760	56.01	15.75	300
23:00	12.16	0	92440	99410	59.98	15.75	300

Time (Hour)	Overflow Solution				Sulfur Balance		Chlorine Balance		
	[SO ₄ ²⁻] mg/L	[OCl ⁻] 10 ³ mg/L	[Cl ⁻] mg/L	Flow gal/hr	d[H ₂ S] gmoles/hr	d[SO ₄ ²⁻] gmoles/hr	d[OCl ⁻] gmoles/hr	d[Cl ⁻] gmoles/hr	*Calc d[OCl ⁻] gmoles/hr
13:00	3860	2.75	20000	346.75	46.59	52.78	155.93	433.30	209.96
17:00	3690	0.95	14200	321.74	79.56	46.81	43.87	392.06	227.29
18:00	3640	0.99	14600	345.72	98.38	49.62	223.04	177.29	256.39
19:00	3620	1.23	15200	342.68	108.89	48.92	171.06	257.42	264.81
22:00	4540	1.12	19500	371.76	132.39	66.55	352.61	183.20	343.87
23:00	4200	1.73	17200	375.73	126.46	62.22	359.75	53.33	324.89

*Calc. OCl⁻ is the amount of OCl⁻ that should be consumed if sulfur is a co-product of the reaction along with sulfate ions, according to equation (31).

NOTES:

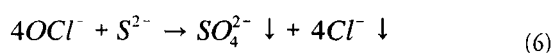
1. Air phase H₂S was read from continuous monitoring system.
2. NaOCl feeding was tested twice at 3:40 pm and 11:00pm and other points were interpolated assuming that the deterioration rate of NaOCl and total concentration of chlorine species CT (Cl) were constant.

except for a newly estimated design inlet H_2S level of 250 ppm. The average air inlet H_2S level (expressed as TRS) and the corresponding removal rate of scrubber #3 in 1996 are shown in the first three columns of Table 3. As indicated, improved scrubber performance has been achieved in the scrubber, which now removes 99% of H_2S , and about 75%- 80 % NMHC, on average. It should be noted that some scrubber inlet air has been bypassing the scrubbers because of faulty butterfly valve dampers. Resolution of that problem is under way.

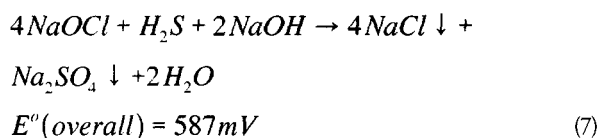
THEORETICAL BACKGROUND

Reaction Chemistry

The operation of odor control scrubbers follows the principle of absorption followed by chemical reaction. Hydrogen sulfide molecules in the incoming air transfer from the gaseous phase into the liquid phase by physical mass transfer. In the liquid phase, the hydrogen sulfide molecules instantaneously break down into hydrogen and sulfide ions, under the influence of the prevailing high pH. The oxidant sodium hypochlorite molecules also exist in completely ionized form in the high pH aqueous phase. The hypochlorite and sulfide ions react with each other through the redox reaction represented by Equation (6).

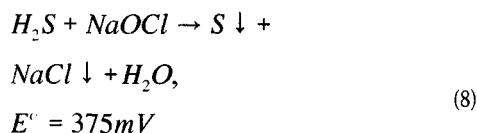


Equation 7 represents the overall reaction.



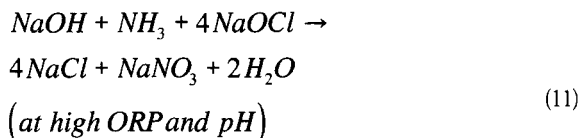
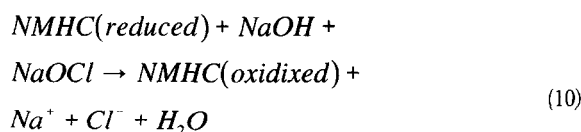
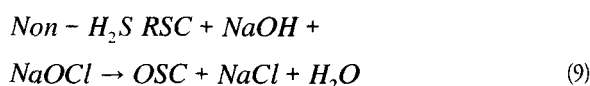
Eight (8) electrons are involved in this redox reaction. E^o represents the theoretical standard ORP per mole of hydrogen sulfide. The original ORP control set point was 450 - 550 mV. This has been increased to 600 mV to achieve complete oxidation of the sulfide ions to sulfate ions.

The reaction [Eqn. (7)] induces a complete oxidation of sulfur from -2 oxidation state to the maximum possible oxidation state of sulfur, +6. However, a partial oxidation of sulfur, from -2 oxidation state to 0 oxidation state (elemental sulfur) is also possible using sodium hypochlorite. This redox reaction can be represented by Equation (8). Two electrons are involved and the standard ORP for this reaction is 375 mV.



If the complete oxidation of hydrogen sulfide to sulfate cannot be achieved, it may be due to limitations in the scrubbing process (e.g. inadequate supply of sodium hypochlorite oxidant solution), limitation in reaction kinetics and/or rate of mass transfer between the aqueous and gas phases in the scrubber (not enough contact time), or depletion of the OCl^- in the liquid boundary layer leading to sulfur precipitation even though the bulk liquid may have enough OCl^- present.

In addition to hydrogen sulfide, some other minor constituents are also oxidized to a limited extent in the scrubber. Some of the representative reactions are given as follows:



where RSC refers to reduced sulfur compounds such as methyl mercaptan, carbon disulfide, dimethyl sulfide, etc. NMHC refers to non-methane hydrocarbons, which represent volatile organics, such as straight-chain and/or branched aliphatic hydrocarbons (with or without chloro-substitution), alkyl substituted aromatic hydrocarbons, etc. Only hydrogen sulfide is regularly monitored, however, because it is by far the major constituent among the gas phase pollutants in wastewater treatment plant air.

Interphase Mass Transfer

The odor control process in a scrubber can be modeled as an interphase mass transfer problem in the light of the classical two film theory. The results of a two film model are fairly accurate, and are adequate for purposes of engineering calculations. The overall redox reaction is assumed to be instantaneous. The following theoretical treatment for the odor control process has been performed utilizing the Danckwerts [4] model for analyses of problems involving mass transfer followed by chemical reaction.

Figure 3 depicts the liquid film and the steady state concentration profiles of the reacting chemicals within the liquid film. Also, for simplicity, the reacting chemicals are treated as their molecular species, instead of as ionic species. The hydrogen sulfide molecules transport from the bulk gas phase (not shown here), through the gas side film and on to the liquid side film. The plane on the left (passing through $x=0$) of Figure 3 represents the gas-liquid film interface. P_{H_2S} and $P_{H_2S}^*$ are the bulk gas phase and the two film interface hydrogen sulfide partial pressures, respectively. $C_{H_2S}^*$ is the concentration of hydrogen sulfide in the liquid film in equilibrium with $P_{H_2S}^*$ at the film interface (which corresponds to A^* in Figure 3). C_{NaOCl} is the bulk liquid phase concentration of sodium hypochlorite (which is represented by B^o in Figure 3). The interface between the liquid film and the bulk liquid has a thickness of δ and is located at $x = \delta$. The plane on which the reaction between the two chemicals occurs is located within the liquid film at a distance δ' from the plane $x=0$, as shown in the figure. Because the two chemicals are reacting, and are being consumed and converted into the product species on this plane, the concentrations of both of them are zero here.

If there were no chemical reaction, and mass transfer by only physical absorption, the hydrogen sulfide molecules would not be destroyed in the liquid film and there would be a finite concentration of hydrogen sulfide in the bulk liquid phase. If that concentration is assumed to be C_{H_2S} and the liquid film side mass transfer coefficient designated as k_L , the steady state physical mass transfer rate per unit packing surface area would be expressed as Equation (12).

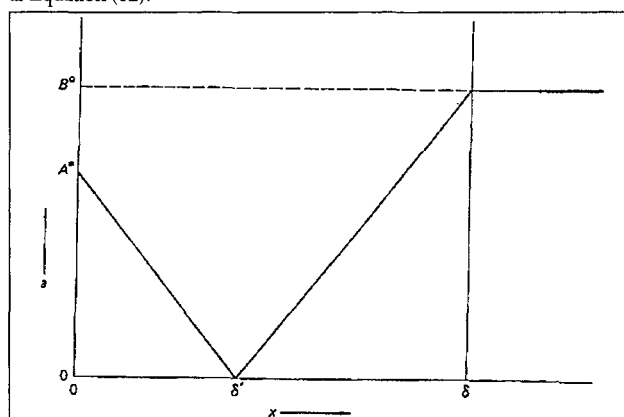


FIGURE 3. Concentration profiles for instantaneous reaction according to film model [4]. © 1970 McGraw-Hill Companies.

$$R = k_L (C_{H_2S}^* - C_{H_2S}) \quad (12)$$

However, because the physical transfer is followed by chemical reaction in this case, the bulk liquid phase hydrogen sulfide concentration, C_{H_2S} , is zero. Moreover, the physical mass transfer coefficient k_L is also enhanced significantly, due to chemical reaction, by a factor E . Because of these effects, the removal of hydrogen sulfide molecules by chemical reaction, in this case, is much faster than by physical absorption only, although it is possible to remove hydrogen sulfide from air by physical absorption alone by using a suitable solvent (e.g. water). The rate of mass transfer, followed by instantaneous chemical reaction, can be expressed as Equation (13).

$$R = k_L E C_{H_2S}^* \quad (13)$$

where E is the enhancement factor.

Hydrogen sulfide and sodium hypochlorite molecules travel from opposite directions toward the reaction plane at $x=\delta'$ to meet each other and react. Under steady state conditions, these two rates are equal. The rate of removal of product molecules from the reaction plane away to the bulk liquid phase also has to be the same as the above rate, or else there would be localized accumulation of product molecules in the system. When all of these rates are expressed in mathematical forms, and equated with one another, the value of the enhancement factor can be obtained (Danckwerts [4]) by Equation (14) [4].

$$E = 1 + (1/z) \left(\frac{D_{NaOCl}}{D_{H_2S}} \right) \left(\frac{C_{NaOCl}}{C_{H_2S}^*} \right) \quad (14)$$

where z is the stoichiometric coefficient of the reaction, and is equal to 4 in the reaction between hydrogen sulfide and sodium hypochlorite. The 'D' terms indicate diffusivities of the respective chemical species.

Since the rate of transport of hydrogen sulfide molecules from the bulk gas phase through the gas side film is the same as the rate through the liquid side film under steady state, the expressions for the two rates can be equated, as follows [4]:

$$\begin{aligned} R &= k_G (P_{H_2S} - P_{H_2S}^*) \\ &= k_L E C_{H_2S}^* \\ &= k_L C_{H_2S}^* \left\{ 1 + (1/z) \left(\frac{D_{NaOCl}}{D_{H_2S}} \right) \left(\frac{C_{NaOCl}}{C_{H_2S}^*} \right) \right\} \\ &= k_L \left\{ C_{H_2S}^* + \left(\frac{D_{NaOCl}}{D_{H_2S}} \right) \left(\frac{C_{NaOCl}}{Z} \right) \right\} \end{aligned} \quad (15)$$

where k_G and k_L are the gas and liquid side mass transfer coefficients of H_2S , respectively. The hydrogen sulfide molecules at the interface are under gas-liquid phase equilibrium. Applying Henry's Law, the partial pressure of hydrogen sulfide can be related to the equilibrium concentration by the following expression:

$$P_{H_2S}^* = H \cdot C_{H_2S}^* \quad (16)$$

where H = Henry's Law Const. for H_2S between air and water phases. The Henry's Law constant H of Equation (16) and H_A , as mentioned in the section on Properties of Hydrogen Sulfide are essentially the same. H is based upon the liquid phase concentration of hydrogen sulfide in terms of moles/liter, whereas H_A uses the equilibrium liquid phase mole fraction.

Using Equation (15), the interface partial pressure of hydrogen sulfide can be further simplified [4].

$$P_{H_2S}^* = H \cdot C_{H_2S}^* = \frac{H \left\{ k_G \cdot P_{H_2S} - k_L \left(\frac{D_{NaOCl}}{D_{H_2S}} \right) \left(\frac{C_{NaOCl}}{Z} \right) \right\}}{(H \cdot k_G + k_L)} \quad (17)$$

and

$$R = \left\{ P_{H_2S} + H \left(\frac{D_{NaOCl}}{D_{H_2S}} \right) \left(\frac{C_{NaOCl}}{Z} \right) \right\} / \left(\frac{H}{k_L} + 1/k_G \right) \quad (18)$$

In Equation 17, the equilibrium partial pressure and concentration of hydrogen sulfide, $P_{H_2S}^*$ and $C_{H_2S}^*$ at the gas-liquid interface both become zero, if the term $\{k_G \cdot P_{H_2S} - k_L (D_{NaOCl}/D_{H_2S})(C_{NaOCl}/z)\}$ becomes zero, which means [4]:

$$k_G \cdot P_{H_2S} = k_L \left(\frac{D_{NaOCl}}{D_{H_2S}} \right) \left(\frac{C_{NaOCl}}{Z} \right) \quad (19)$$

and

$$P_{H_2S} = k_L \left(\frac{D_{NaOCl}}{D_{H_2S}} \right) \left(\frac{C_{NaOCl}}{Z} \right) / k_G \quad (20)$$

This happens to be the case when the reacting surface merges with the gas-liquid interface, and the result is that the rate of mass transfer of hydrogen sulfide from the bulk gas phase through the gas film to the interface exactly matches the rate of transfer of stoichiometric amounts of sodium hypochlorite through the liquid film to the interface. This situation is depicted by concentration profile 4 b of Figure 4.

When the resistance to mass transfer is higher in the liquid side than in the gas side, hydrogen sulfide molecules have to travel further into the liquid side film to come into contact with sodium hypochlorite molecules in stoichiometric amounts for Reaction 7 to occur. In this case, the right hand side of Equation 20 [4] is less than the left hand side. This situation is depicted by profile 4 a

When the gas side resistance is higher than the liquid side resistance, the sodium hypochlorite reaches the reacting plane faster than hydrogen sulfide, and there is also a residual concentration of sodium hypochlorite at the reacting plane due to a transfer rate of sodium hypochlorite higher than stoichiometric

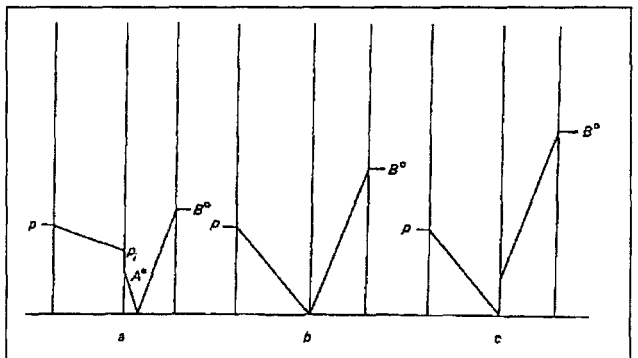


FIGURE 4. Two film model: concentration profiles for instantaneous reaction with varying film resistances [4].

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metric. In this case, the right hand side of Equation (19) is greater than the left hand side, and the reaction rate is expressed as $R=k_G \cdot P_{H_2S}$. This situation is depicted by profile 4 c.

This theoretical treatment has been kept simple by making the following assumptions.

1. The mass transfer of sodium hypochlorite and hydrogen sulfide takes place in molecular, not ionic forms.
2. No thermal effects are associated with these reactions.
3. The modeling does not consider the effect of solids deposition on the packing medium, which makes it a moving boundary, as opposed to a fixed boundary problem.

Scrubber Sizing

For the case of hydrogen sulfide oxidation by sodium hypochlorite solution, the entire resistance to mass transfer can be assumed to be lumped into the gas side at low concentrations of hydrogen sulfide, typically below 25 ppm. In such a case, the gas side rate is the rate-limiting step to the overall rate of mass transfer, and the rate is expressed as $R=k_G \cdot P_{H_2S}$, as shown in the previous section. As explained before, this is the transfer rate per unit surface area of packing material, i.e. the mass transfer surface. Considering a thin vertical element, of differential height 'dh' of the scrubber cross-section, and assuming it to be at an equilibrium stage, the rate of mass transfer per unit cross-sectional area of the scrubber can be equated with the number of moles of hydrogen sulfide oxidized within that element, as follows:

$$k_G \cdot a \cdot P_{H_2S} \cdot dh = d(G \cdot y_{H_2S} / M) \quad (21)$$

where

G= mass velocity of the gas phase entering the differential element at the bottom,

M= molecular weight of the gas phase
and

y_{H_2S} = mole fraction of H_2S in the gas stream entering the differential element.

Each term on the right hand side is a variable. However, for a dilute gas stream, where the solute gas (H_2S) is present in ppm levels in both inlet and outlet of the scrubber, the values of G and M can be very closely approximated by those of the inert component in the gas phase, which is air, and thus can be treated as constants.

On the other hand, the partial pressure term, P_{H_2S} , on the left hand side can also be expressed as a product of the gas phase total pressure, P_t , in the scrubber, and the mole fraction of hydrogen sulfide, y_{H_2S} , in the gas phase. Under normal operating conditions, the gas side pressure drop across the total height of the scrubber is very low, and hence P_t can be considered constant. The hydrogen sulfide mole fraction, y_{H_2S} , is, however, a variable along the entire height of the scrubber.

Considering the above conditions, Equation (21) can be simplified as follows:

$$k_G \cdot a \cdot y_{H_2S} \cdot P_t \cdot dh = G/M \cdot d(y_{H_2S})$$

or,

$$dh = [G/M \cdot k_G \cdot a \cdot P_t] \cdot [d(y_{H_2S})_2 / (y_{H_2S})_1]$$

Integrating both sides under the terminal conditions of $y_{H_2S} = (y_{H_2S})_1$ at $h = 0$ (scrubber inlet), and $(y_{H_2S})_2$ at $h = H_t$ (scrubber outlet), the following expression is obtained:

$$H_t = \left[G / M \cdot k_G \cdot a \cdot P_t \right] \cdot \left[\ln \left\{ (y_{H_2S})_2 / (y_{H_2S})_1 \right\} \right] \quad (22)$$

Equation (22) [5] is the design equation to determine the packing height of an odor control scrubber when the air flow rate, the total air pressure, the hydrogen sulfide concentration, and the desired scrubber outlet hydrogen

sulfide concentration (or the desired hydrogen sulfide removal efficiency of the scrubber) are defined. The molecular weight term, M, for air is a known constant. The terms k_G and 'a' are system specific. Empirical equations to determine the mass transfer coefficient, k_G are available, but the results obtained from such relations are not very reliable, and it is therefore normally obtained from representative bench or pilot scale runs. The value of 'a' is packing type and material specific. In industry wide design practice, these two parameters are obtained from the packing vendor's proprietary information. Sometimes the vendors provide the entire first term, which is the Height of a Transfer Unit (HTU) for the gas-liquid system. The second term, which is the Number of Transfer Units (NTU), can be easily calculated from the known value of the inlet concentration and the desired value of the outlet concentration of hydrogen sulfide. Thus, the packed height of the scrubber can be determined by multiplying the values of HTU and NTU.

The other dimension is the scrubber diameter. For any packed gas-liquid contact equipment, standard correlations between gas and liquid mass flow rates, transport properties, and pressure drop across the packed height for various gas and liquid loading conditions are available in graphical form [6]. These graphs are also packing specific, and must be obtained from the packing manufacturers' reference literature. For a given gas flow rate and inlet concentration of hydrogen sulfide, the first step is to calculate the required liquid flow rate from the overall oxidation stoichiometry, as derived from Equation (7). The next step is to obtain from the graphs the corresponding mass velocity of the gas phase through the column, operating at a condition safely below flooding. Finally, from the gas phase mass velocity and mass flow rate data, the column cross-sectional area, and hence the column diameter, can be calculated.

OPERATIONAL EXPERIENCE AT DEER ISLAND

As mentioned earlier, Scrubber #3, which, among all the odor control scrubbers on Deer Island, apparently experiences the maximum hydrogen sulfide inlet concentrations, was modified to accommodate higher flow rates of the absorbent solutions of sodium hypochlorite and sodium hydroxide. A one-day field testing program was undertaken to better understand the effect of the above mentioned modification of Scrubber #3. The test results, shown in Tables 3, indicate findings from an attempt to perform a set of material balances of the various reactant and product species entering and leaving the scrubber. The background information on the procedure for analysis of the data obtained from the field test is presented below.

Material Balance Basis

Within the scrubber system, the material balance for a given chemical species can be expressed, in the most general terms, as follows:

Rate of Moles In - Rate of Moles Out + Rate of Generation Due to Reaction = Rate of Accumulation

Under steady state operation, the right hand term becomes equal to zero. This basis has been used to account for the gain or loss of individual chemical species, as described below.

Material Balance for H_2S :

Hydrogen sulfide depletes within the scrubber due to reaction. Therefore, for hydrogen sulfide, the equation takes the form:

Moles of H_2S in Scrubber Inlet Air - Moles of H_2S in Scrubber Outlet Air - Moles of H_2S Reacted in Scrubber = 0.

Assuming no other source or sink of hydrogen sulfide in the system, the above equation can be rewritten as:

$$Q_{G1} \cdot (y_{H_2S})_1 - Q_{G2} \cdot (y_{H_2S})_2 = \Delta [H_2S] \quad (23)$$

where Q_G and y_{H_2S} represent the molal gas phase flow rates and mole fractions of hydrogen sulfide in the gas phase respectively, subscripts 1 and 2 indicate scrubber inlet (bottom) and outlet (top) conditions, and $\Delta [H_2S]$ repre-

sents depletion of the number of moles of hydrogen sulfide in the gas phase, from scrubber inlet to outlet.

Material Balance for SO_4^{2-} :

Sulfate ions are generated within the scrubber as a result of reaction 7. Following the same procedure as for hydrogen sulfide, the material balance for sulfate ions can be expressed as:

$$\Delta[SO_4^{2-}] = Q_{L1} * C_{SO4(1)} \quad (24)$$

where Q_{L1} is the volumetric flow rate of overflow liquid from the scrubber bottom sump, $C_{SO4(1)}$ is the molar concentration (moles per unit volume) of sulfate ions in the bottom sump, and $\Delta[SO_4]$ is the moles of sulfate ions formed due to reaction 7.

Material Balance for OCl^- :

Fresh make-up sodium hypochlorite, supplied to the scrubber as a 15% aqueous solution, exists as hypochlorite ions under the highly alkaline pH condition. If the feed rate of sodium hypochlorite solution to the top of the scrubber is defined as Q_{L2} then the material balance for hypochlorite ions can be expressed as follows:

$$Q_{L2} * (C_{OCl-(2)}) - Q_{L1} * (C_{OCl-(1)}) = \Delta[OCl^-] \quad (25)$$

where $C_{OCl(2)}$ and $C_{OCl(1)}$ are the concentrations of hypochlorite ions in the liquid phase at the scrubber inlet (top for liquid phase) and outlet (sump overflow) respectively. $\Delta[OCl^-]$ is the decrease in number of moles of hypochlorite ions from the top to the bottom of the scrubber.

Material Balance for Cl^- :

Chloride ions are formed as a result of reaction 7. The material balance equation for chloride ions can be expressed as:

$$Q_{L1} * (C_{Cl-(1)}) - Q_{L2} * (C_{Cl-(2)}) = \Delta[Cl^-] \quad (26)$$

where, $C_{Cl(1)}$ and $C_{Cl(2)}$ are the concentrations of chloride ions in the fresh sodium hypochlorite solution inlet at the top of the scrubber and at the bottom sump, respectively. $\Delta[Cl^-]$ is the increase in the number of moles of chloride ions from the top to the bottom of the column as a result of reaction 7. It is assumed that there is no other source or sink of chloride ions.

Stoichiometric Relations:

The following relationships can be obtained from the stoichiometry of reaction 7 if hydrogen sulfide is completely oxidized into sulfate.

$$\Delta[OCl^-] = \Delta[Cl^-] \quad (27)$$

$$4\Delta[OCl^-] = \Delta[H_2S] \quad (28)$$

$$\Delta[SO_4^{2-}] = \Delta[H_2S] \quad (29)$$

However, if hydrogen sulfide is partially oxidized to sulfur, according to reaction 8, Equations (28) and (29) become invalid, and the stoichiometric relationship becomes:

$$\Delta[OCl^-] = \Delta[H_2S] \quad (30)$$

Field Test Program and Data Collection

The test program consisted of collecting process information on the gaseous and liquid phases of the scrubber #3 inlet and outlet streams. Six sets of data were collected during the one day test program. Each set includes the air flow rate through the scrubber, inlet and outlet TRS concentrations in terms of parts per million (ppm), and the inlet and outlet NMHC concentrations in terms of ppm. These data were retrieved directly from the automatic continuous emission monitoring system (CEMS) of the scrubber. At the same times, liquid samples were collected from the scrubber overflow and analyzed for concentrations of chloride, hypochlorite, and sulfate ion concentrations.

The liquid phase entering the scrubber at the top consists of three components; the 15% aqueous solution of sodium hypochlorite, the 50% aqueous solution of sodium hydroxide, and make-up water to maintain the sump level. The make-up water rate is continuously monitored by a flow meter, which automatically transmits the information to the plant-wide distributed control system (DC S) network for data storage. The sodium hydroxide and hypochlorite solution feeding rates were obtained from the stroke length and speed of individual pumps.

The trailer mounted CEMS consists of a Meloy SA 1 85-2A flame photometric detector (FPD) based TRS analyzer and a Byron Model 301 GC/FID based NMHC analyzer, with the provision of continuously withdrawing air samples from the inlet and the outlet of the test scrubber.

For the liquid samples, the sulfate ion analyses were performed by using ion chromatographic technique (EPA Method 300-0), with the help of a Dionex, Model DX 500, Ion Chromatographic System. Hypochlorite ions were analyzed by iodometric titration, using sodium thiosulfate as the titrant and starch indicator (Standard Methods 4500-Cl-B). Chloride ions were analyzed by silver nitrate titration method (Standard Methods 4500-Cl-D) using a Mettler DL 70 autotitrator. Summarized raw data and calculated results are presented in Tables 2 and 3.

RESULTS AND DISCUSSIONS

Table 2 presents the removal efficiencies of total reduced sulfur (TRS). Because hydrogen sulfide is by far the most predominant compound (>95%), for purposes of data analysis and interpretation the TRS data is used for quantification of hydrogen sulfide removal. Analytical results of the feed and overflow liquid streams, as well as the calculated results, are presented in Table 3. In Table 3, the four columns of dH_2S , dSO_4 , dCl^- , and $dOCl^-$, represent the difference in the number of moles of each of these species between the inlet and the outlet of the scrubber, as calculated from the liquid flow rate and the terminal concentrations. The last column, $CaIc. dOCl^-$, is explained later.

It may be observed from these Tables that the overall removal efficiency of hydrogen sulfide by the scrubber system is always well above 99%, even with the highest inlet loading of about 68 ppm (which was observed to be the highest during the test period). However, it can also be observed that the concentration of sulfate ions in the sump, which directly indicates the amount of completely oxidized hydrogen sulfide, does not increase correspondingly to the increase of hydrogen sulfide load into the scrubber and the simultaneous rise of the sodium hypochlorite feed rate. Primarily all the hydrogen sulfide can be completely oxidized into sulfate when the inlet H_2S load is up to 5 lb/hr (H_2S level at 25ppm at the air flow rate of 33,000 scfm). When the inlet H_2S load is above that, even though the overall removal of H_2S is still above 99%, only partial amounts, to the extent of approximately 50%, can be completely oxidized into the final product sulfate ions. It can be easily noticed from the columns for dH_2S and dSO_4 in Table 3 that Equation (29) for complete oxidation of sulfur is not fulfilled, and H_2S balance closure is not achieved when the hydrogen sulfide influent load is above approximately 5 lb/hr (25 ppm). This is also graphically depicted in Figure 5, which is a plot of the values of dH_2S of Table 3 against the values of dSO_4 . This points out an upper limit of capability of the H_2S - $NaOCl$ - $NaOH$ scrubber to completely oxidize hydrogen sulfide into sulfate, even if the system control para-

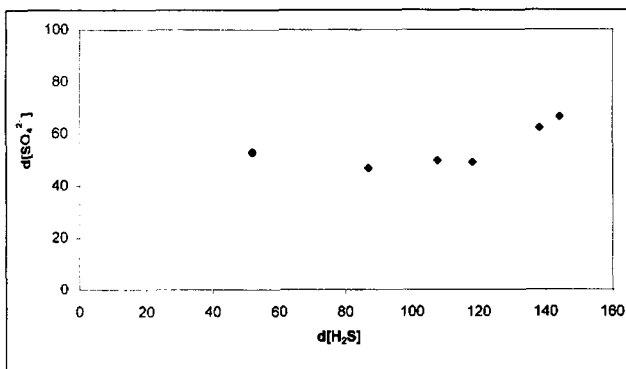


FIGURE 5. Plot of sulfate ions formation versus hydrogen sulfide removal across the scrubber.

meter pH and ORP values are maintained constant by adjustment of the NaOCl and NaOH feeding rates.

Of all the H_2S that was removed through the scrubber, supposing that the part not oxidized into sulfate ions was oxidized into sulfur as in Equation (8), the stoichiometric balance for hypochlorite ions changes to the following instead of that expressed by Equation (28).

$$\Delta[OCI^-] = 4 * \Delta[SO_4^{2-}] + (\Delta[H_2S] - \Delta[SO_4^{2-}]) \quad (31)$$

The calculated values in the left hand term of the above equation are presented in the last column of Table 3, under the title Calc. $dOCI^-$. The mass balance of hypochlorite ions can be followed by comparing the numbers in the column for $dOCI^-$ with the corresponding numbers in the column for Calc $dOCI^-$ in Table 3. The correspondence is shown graphically in Figure 6. Although the numbers ($dOCI^-$ and corresponding Calc. $dOCI^-$) are not equal, as they should be ideally, they are observed to be quite close to each other except at 17:00 hrs. (5:00 PM). The error may be due to experimental errors in the chloride and hypochlorite determination processes, and the deterioration of hypochlorite solution concentration during testing.

The observation of a considerable amount of yellow particles of sulfur in the sump overflow in the West Odor Control scrubber system in the summer, when the hydrogen sulfide level was high (25 ppm-200 ppm), agrees with the above analysis that elemental sulfur will be a co-product if the hydrogen sulfide load is above 5 lb/hr (H_2S level at 25 ppm). The extent of disagreement between the two abovementioned columns of Table 3 is anticipated to be primarily due to the following reasons:

1. TRS data has been used for hydrogen sulfide concentrations. In reality, additional hypochlorite ions are consumed in the oxidation of other sulfur compounds, e.g. mercaptans, disulfides, etc.

2. Additional amounts of hypochlorite ions are consumed to oxidize, partially or fully, the various non methane hydrocarbon molecules present in the air.

3. Sodium hypochlorite solutions continuously degrade. The concentration of hypochlorite was not checked at every data point; instead it was estimated by linear interpolation between two points.

4. Some amount of uncertainty and error may be involved in the various instrumental analysis methods for different chemical species.

5. The tests were not performed under the best controlled conditions, and some amount of uncertainty in the results is expected.

These results indicate that even after increasing the capacity of dosing pumps and feeding stoichiometric quantities of sodium hypochlorite, complete oxidation of the influent hydrogen sulfide could not be achieved. This happens even though there is sufficient packing height available in the scrubber to provide the necessary time for complete oxidation of hydrogen sulfide.

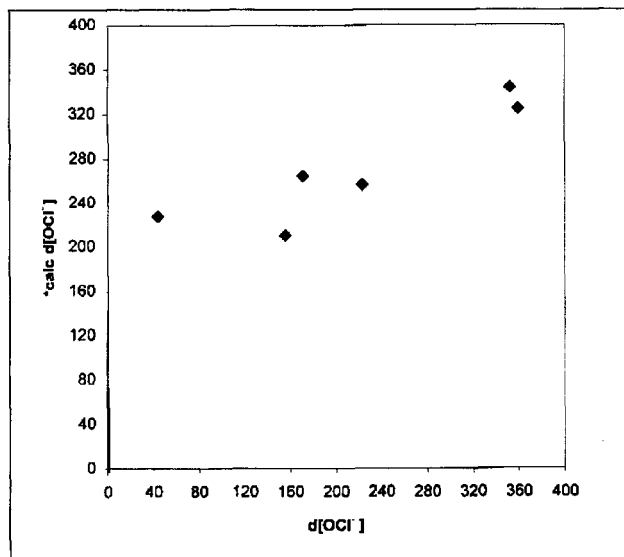


FIGURE 6. Plot of actual versus theoretical depletion of hypochlorite ions across the scrubber.

According to Equation (22), the scrubber height required is 7.84 feet, to completely oxidize (to sulfate) a very high inlet hydrogen sulfide concentration of 250 ppm, to the extent of 99.5% from the air stream entering the scrubber at the rate of 40,000 scfm. This result is based upon an HTU value of 1.48 feet, calculated from a vendor supplied empirical equation for the corresponding liquid and gas flow rates in the scrubber. The NTU value of 5.30 was calculated based upon the removal efficiency (99.5%) of hydrogen sulfide from the air entering the scrubber. Thus, the provided packing height of 10 feet should have been more than the height required to remove the incoming hydrogen sulfide by complete oxidation to sulfate ions on the day of the test (in which H_2S levels reached a maximum of 68 ppm). However, the partial oxidation to elemental sulfur suggests that the hydrogen sulfide removal process in the H_2S -NaOCl-NaOH scrubber becomes mass transfer limited and the liquid film resistance becomes a significant factor in the overall mass transfer coefficient beyond a certain concentration of influent hydrogen sulfide in air. This causes a significant reduction in the value of the overall process mass transfer coefficient k_g . In light of the Danckwerts model, referring to Figure 4, it can be stated that above the inlet hydrogen sulfide concentration of 25 ppm, the concentration profile shifts from 'c,' to 'b,' to 'a.' This limitation is enhanced further with the deposition of product solids on the packing surface, resulting in the reduction of packing surface area 'a' in Equation 22. Moreover, this shifts the simple gas-liquid mass transfer problem into the moving boundary region, where the reactant hydrogen sulfide molecules encounter additional resistance to diffusion through the pores of the solid product layer in order to contact the liquid surface available within the pores.

Potentially, the liquid side mass transfer deficiency could be overcome by using a more concentrated sodium hypochlorite solution, which might move the liquid side concentration profile 'a' in Figure 4, parallelly upwards to 'b,' or even to 'c.' The main limitation for such a measure is the high degradation tendency of sodium hypochlorite. At concentrations higher than 15%, sodium hypochlorite solutions degrade very rapidly and have a very short shelf life. Deer Island obtains sodium hypochlorite solution from vendors by barge once every two to three weeks, whence it is stored in tanks and continuously consumed. Therefore, increasing the solution concentration is not an option for Deer Island unless the storage time is minimized by generating the hypochlorite on-site, or receiving it more frequently. On-site generation of sodium hypochlorite is currently under review.

Appropriate actions to enhance scrubber performance appear to include improving liquid-gas mass transfer conditions in the scrubber by frequent cleaning of the packing (or changing packing material), and decreasing H_2S

scrubber inlet concentrations to below 25 ppm. Deer Island has taken several recent steps in those directions. Routine washing of packing material has been initiated during the Fall of 1997. A trial basis pretreatment program of Deer Island influent wastewater was successful during the previous summer using several dosing chemicals. Full scale pretreatment of Deer Island influent with sodium hypochlorite was initiated last summer. Full scale pretreatment facilities for hydrogen peroxide has been recommended for design. However, if the scrubber inlet concentration of hydrogen sulfide in air can not be controlled below 25ppm, the other possible alternative is to change the packing materials to achieve better mass transfer characteristics, which should cause a reduction in the gas side film resistance.

CONCLUSION

Hydrogen sulfide may not be completely oxidized by sodium hypochlorite solution into the final product of sulfate ions if the scrubber inlet H₂S load is above some threshold value, which depends upon the configuration of the scrubber and the packing material. For the Deer Island Treatment Plant, this value appears to correspond to 25 ppm of hydrogen sulfide. Above this level, sulfur will be a major co-product. Sulfur formation is detrimental to scrubber performance because eventually it chokes up the packing voids, adversely affecting the hydrogen sulfide removal process, and ultimately lead-

ing to escape and emission of partially treated air. Consideration of the effects of sulfur formation on the scrubber, and the cost of operation and maintenance, should be taken into account when evaluating the overall performance of the scrubber odor control system.

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