Experimental Assessment of Water Sprays Utilization for Controlling Hydrogen Sulfide Releases in Confined Space

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This paper reported the utilization of water spray for controlling H$_2$S release in a confined space, which is especially important in industry. A typical spray tower was modified to simulate the confined space for people’s enterable routine operation (e.g., pump room), in which the dilution capacity of water sprays can also be evaluated. This work consists of two parts: the first part focuses on the influences of different operating conditions on chemical dilution capacities of water sprays in mechanisms; the second one is comparison between two nozzle configurations for evaluating their feasibilities of practical application. Water sprays express eligible performance for H$_2$S release control even though their dilution capacity was weakened at high gaseous concentrations and rates of releases. The presence of Na$_2$CO$_3$ can significantly improve absorption effectiveness of H$_2$S in water and the optimal Na$_2$CO$_3$ additive was found to be 1.0 g L$^{-1}$ in this test. Compared with Na$_2$CO$_3$, adjusting water flow rate may be an effective strategy in enhancing dilution capacity of water sprays due to the fact that larger flow rate led to both less dilution time ($T_D$) and dilution concentration ($C_D$). Furthermore, multinozzle configuration is more efficient than single-nozzle configuration under the same water consumption.

1. Introduction

A variety of factory employees are killed or seriously injured each year in confined space due to accidental releases of hydrogen sulfide (H$_2$S). A small limited space which receives minimal ventilation is conducive to the accumulation of hazardous gases and can constitute serious detriments to laborers once the accident occurred. An example is the pump room of wastewater treatment plant (WWTP), in which the emissions of H$_2$S commonly occur because of pipelines corrosion and irregular operation. The consequences will be disastrous especially when a high concentration gaseous release of H$_2$S takes place. It is known that inhalation of H$_2$S higher than 1000 ppm can cause an instantaneous death after a few breaths. Although worker security in process areas has been extensively improved with installation of toxic gas monitors (e.g., E-nose system) [1, 2], further studies in the development of reliable mitigation devices are still necessary. So far, however, the effective resolutions for controlling accidental release of H$_2$S in confined space remain deficient.

Although the dispersion of hazardous clouds can be controlled by a lot of techniques such as thermal inactivation, fans, and specific foams, they are technically and economically unviable for utilization in the confined space [3, 4]. Water spray, by contrast, is suitable for both of the confined and unconfined spaces.

The dilution/dispersion capacity of water sprays has been studied for many years [5–9]. It can improve the dilution/dispersion rate of these hazardous components in air, by means of the subsequent mechanisms (containment action, diluting action, and physical and chemical absorption) [5, 10]. In general, two kinds of technical solutions can be selected for dealing with different nature of gases. One is the use of fresh water sprays for water-soluble gases, such as ammonia (NH$_3$) and hydrogen fluoride (HF); the other one is the use of doped water sprays with alkaline additives for less-soluble gases, such as H$_2$S and chlorine (Cl$_2$). The second solution has not always been studied with regard to the water and soil contamination involved [11]. Nevertheless, the use of the first solution on mitigation of Cl$_2$ has been
proved to be inefficient without chemical additives [12]. As for H$_2$S, it is more difficult to dissolve in water than Cl$_2$. Hence, the use of alkaline additives is imperative to promote the mass transfer from the gaseous phase to the liquid one [13]. Various alkalis (e.g., sodium hydroxide (NaOH), sodium hypochlorite (NaOCl), sodium carbonate (Na$_2$CO$_3$), and sodium bicarbonate (NaHCO$_3$)) are able to remove H$_2$S after having been added in the liquid phase. The most frequently used is Na$_2$CO$_3$ due to low cost, ecofriendliness, efficiency, weak corrosion, and irritation to the skin.

Herein, systematic tests were carried out to assess the dilution capacity of water sprays utilization for mitigating H$_2$S releases occurring in a confined space. Both dilution time ($T_D$) and dilution concentration ($C_D$) were proposed as the measurement of water spray effectiveness. The first part of this paper is to investigate the influences of different experimental parameters on the dilution capacity. The second part illustrates the improving dilution capacity of water sprays by using multinozzle configurations.

2. Experimental Sections

2.1. Modified Spray Tower. A classic spray tower was modified to evaluate the applicability of water sprays for controlling H$_2$S releases in a confined space. This device was comprised of a column cavity equipped with water supply and water spray nozzles, as well as the H$_2$S source and gas detectors, as illustrated in Figure 1(a).

2.1.1. Column. The forced dispersion of H$_2$S was carried out in the Plexiglas column with internal diameter of 0.6 m, height of 1.5 m, and wall thickness of 15 mm against H$_2$S corrosion. Besides the gas-liquid space, the column also afforded the locations for H$_2$S release, spray nozzles, and gas detection.

2.1.2. H$_2$S Source. The integration of cylinder of H$_2$S (0.49%, 10 bars) and cylinder of compressed air (10 bars) can achieve a steady gaseous release and was employed as H$_2$S source. The mixed H$_2$S gas was eventually released into the column through the stainless steel tube located at the height of 10 cm above the bottom. In addition, a cover was used to prevent droplets from falling into the intake tube (Figure 1(b)). The steady releases were inspected by means of the dynamic multiple gases distributing system (DMGDS, MF-5B, China), which endowed a good repeatability of gas flow rate ($\geq 95.5\%$) and a small relative error of gas concentration ($\leq 1.5\%$).

2.1.3. Water Supply and Water Spray Nozzles. The downward spray nozzles were fixed at the top of the column. As shown in Figure 1(c), four nozzles were situated symmetrically around the central one. Na$_2$CO$_3$ solution was stored in the tank and transported into the spray nozzles through the magnetic pump (CQB15-10-85F, China). Water flow rates were measured by a turbine flow meter (LWGYS-C, China).

During the tests, a number of full cones (QDBB, China) were used to create two nozzle configurations. One involves the simultaneous use of a set of four same surrounding nozzles and the other one contains a single central nozzle. All these special spray nozzles were mainly characterized by flow rates and angles (Table 1). The water flow rate represented
Table 1: Spray nozzles main characteristics.

<table>
<thead>
<tr>
<th>Spray nozzle configurations</th>
<th>Spray pattern</th>
<th>Water flow rate per nozzle (×10⁻³ m³ s⁻¹)</th>
<th>Spray angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>One-nozzle set</td>
<td></td>
<td>0.83</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.6</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.3</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.0</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6.7</td>
<td>30</td>
</tr>
<tr>
<td>Four-nozzle set</td>
<td></td>
<td>1.6</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.3</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6.7</td>
<td>15</td>
</tr>
</tbody>
</table>

2.1.4. Gas Detection. A circular measurement network with the H₂S leaking point (a stainless steel pipe) at the center of the circle was used throughout the tests. Four gas sampling points were symmetrically distributed on the wall of column at a height of 0.4 m above the bottom to establish the dilution capacity on four transects running different directions from the leaking point. Instead of the respiration, diluted H₂S was pumped at 2.5 × 10⁻⁵ m³ s⁻¹ into the flexible pipe connected with a H₂S analyzer (MultiCheck 2000, America). This analyzer can meet the requirements of evaluation with a measurement accuracy of ±0.1 ppm reading in the range of 0 to 500 ppm.

2.1.5. Exhaust System. The column needed to be cleaned up at the end of each test, with the exhaust system including an air compressor and gas absorber. With the help of air compressor (Dynair, DA7001, China), retained H₂S was blown into an alkali liquor-filled absorber through the gas outlet on the top of column (Figure I(c)).

2.2. Procedure. The principal of the lab-scale tests conducted was to release H₂S into a confined space and to measure the reduction of concentration with water spray operating. More details were shown below. Firstly, a natural release without water sprays operation was passed into the column. Secondly, the water supply system was started once the H₂S concentration in sampling points exceeded 10 ppm (the National Institute for Occupational Safety and Health (NIOSH) recommended a permissible exposure limit of H₂S of 10 ppm at the workplace). During the processes of spraying, the H₂S concentration was recorded at intervals of 10 seconds. Thirdly, when H₂S concentrations decreased to a steady level, the gas inlet and water supply system should be turned off sequentially. It was also worth noting that each test consisted of a natural release and a forced dispersion with water sprays needed to last for approximately 2 minutes. Finally, remains of H₂S in column should be removed with the exhaust system at the end of each test so as to continue the next one.

3. Results and Discussion

3.1. The Assessment of Dilution Capacity of Water Sprays. Many previous assessment methods include dilution ratio (DR), forced dispersion coefficient (FD), and mitigation factor (DF), which were almost defined as the ratio of the free dispersion gas concentration to the concentration in presence of spraying [3, 5, 7]. These approaches, nevertheless, were limited to the open field instead of enclosed spaces considering an expansive spatial scale for detection. Given this, dilution time (TD) and dilution concentration (CD) were used to assess the effectiveness of downward water sprays in a confined space, as interpreted in Figure 2.

According to concentration variations, the forced dispersion of H₂S release with water spray can be divided into two stages. The initial unsteady stage, fast dilution stage (DS), was symbolized by the violent fluctuation of H₂S concentration after first contact with droplets. Then the H₂S concentration was constant down to a transitional point. We defined it as critical concentration (CC), where there were no more obvious changes on the variation of H₂S concentration (ΔC ≤ 0.1 ppm). In the second stage, constant DS, the relatively stable H₂S concentration occurred until the absorption balance was ultimately achieved. Therefore, dilution time (TD) can be considered as the duration of the first stage, for the evaluation of dilution rate of water sprays. Since the concentrations variations in constant DS were minimal, it is fine to choose the concentration at 120 seconds as the dilution concentration (CD), which can well demonstrate the absorption effectiveness of water spray. Moreover, Figure 2 also depicts the evolution of H₂S concentration in four orthogonal directions of the same horizontal level. The result reveals the homogeneous dispersion of gas without disturbance (e.g., wind), so measurement of H₂S concentration in any sampling points was of conformity.
3.2. The Influences of Different Parameters on the Dilution Capacity of Water Sprays. Basically, the dilution capacity of water spray depends on its own characteristics (water flow rates, the alkali concentration, etc.); extrinsic parameters include gas nature (concentration) and gas release rates. To analyze the influences of these parameters on the dilution effectiveness of water spray, a series of tests with one-nozzle configuration were performed. The experimental conditions were listed in Table 2.

Table 2: Experimental conditions for parameters tests (one-nozzle set).

<table>
<thead>
<tr>
<th>Inlet H$<em>2$S concentrations $C</em>{H_2S,I}$ (ppm)</th>
<th>Operation conditions</th>
<th>Na$_2$CO$<em>3$ concentrations $C</em>{ab}$ (g L$^{-1}$)</th>
<th>Water flow rates $Q_L$ (m$^3$·s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Test (a) 1000–5000</td>
<td>5 × 10$^{-5}$</td>
<td>1.2</td>
<td>5 × 10$^{-5}$</td>
</tr>
<tr>
<td>Test (b) 3000</td>
<td>5 × 10$^{-5}$–1.7 × 10$^{-5}$</td>
<td>1.2</td>
<td>6.7 × 10$^{-5}$</td>
</tr>
<tr>
<td>Test (c) 3000</td>
<td>8.3 × 10$^{-5}$</td>
<td>0–1.2</td>
<td>6.7 × 10$^{-5}$</td>
</tr>
<tr>
<td>Test (d) 3000</td>
<td>6.7 × 10$^{-5}$</td>
<td>1.0</td>
<td>0.8 × 10$^{-5}$–6.7 × 10$^{-5}$</td>
</tr>
</tbody>
</table>

3.2.1. Dilation Time of Water Spray Tested. Figure 3 presents the variation of dilation time ($T_D$) of water spray for different experimental conditions. Remarkably, $T_D$ increased with the inlet H$_2$S configuration ($C_{H_2S,I}$) and gas release rate ($Q_G$) (Figures 3(a) and 3(b)), while it decreased with the increase of water flow rate ($Q_L$) and did not seem to rely on the Na$_2$CO$_3$ concentration ($C_{Na_2CO_3}$) (Figures 3(c) and 3(d)). The most reasonable explanation for these differences of $T_D$ was that the falling droplets induced a violent air flow by acting on their dispersion [5]. In the processes of spraying, the horizontal movement of gas molecule was weakened but vertical movement was strengthened at the same time. Thus this effect could effectively prevent the H$_2$S diffusion to the outside of the “capture zone,” as well as enhancing the opportunities of gas-liquid mass transfer. Virtually, the measurement of air flow commonly used was the Reynolds number (Re), which was defined as the ratio of inertial forces ($f$) to viscous forces ($τ$) [14]. In the current work, the true value of Re was difficult to determine with interference of the fast droplets, but the trends of Re still could be deduced by the following equations:

$$f = u^2 \rho,$$  \hspace{1cm} (1)

$$τ = \frac{u}{d},$$  \hspace{1cm} (2)

$$Re = \frac{f}{τ} = \frac{d \rho u^2}{\mu},$$  \hspace{1cm} (3)

where $f$ is the inertial forces of gas flow, $τ$ is the viscous forces of gas flow, $u$ is the gas velocity, $\rho$ is the density of H$_2$S gas, $\mu$ is the viscosity of H$_2$S gas, and $d$ is the diameter of column.

When $C_{H_2S,I}$ increased, increased, according to (3), Re increased with the combined action of an increase of the gas density since $\rho_{H_2S} (1.385$ Kg·m$^{-3}) > \rho_{Air} (1.169$ Kg·m$^{-3})$ and a decrease of the gas viscosity since $\mu_{H_2S} (1.239$ Pa·s) < $\mu_{Air} (1.845$ Pa·s). And also, Re increased with $Q_G (u)$ on account of (3). Severe turbulence could reasonably result in decreasing of $T_D$; however, $T_D$ extended as we can see in Figures 3(a) and 3(b). It was ascribed to significant enhancement of gas diffusion caused by increasing H$_2$S within confined space, and often this enhancement in field test was easy to be counteracted by unstable atmosphere (e.g., wind). Consequently, the indoor toxic gas releases are more jeopardous for workers than those occurring outdoors. When $C_{Na_2CO_3}$ increased, a decrease of $T_D$ can be observed in Figure 3(c). The effect of Re can be ruled out since it was $C_{Na_2CO_3}$ independent based on (3). Thereby the result arose from the enhancement of absorption in water with the increase of $C_{Na_2CO_3}$. It seemed that the action was very slight to the reduction of $T_D$ (about 10 seconds), but the mitigation was inefficient without the presence of Na$_2$CO$_3$. It could be confirmed by the fact of water curve in Figure 3(c) that the H$_2$S concentration decreased rapidly in the first 60 seconds and then increased again. When $Q_L$ increased, $T_D$ decreased distinctly (Figure 3(d)). The reason was that strengthening gas-liquid collision acted by falling droplets improved the interference of the air flow resulting in the increase of Re.

3.2.2. Absorption Effectiveness. In addition to the dilution time ($T_D$), Figure 3 indicates the variation of absorption effectiveness of water sprays for different experimental conditions as well. Although the change of dilution concentration ($C_D$) was analogous to the variation of $T_D$, the driving force was very different. The gas-liquid mass transfer accompanied with neutralization led to the persistent and efficacious absorption in water. In this study, the volume mass transfer coefficient ($k_{v,a}$ or $k_{v,d}$) was used to characterize the gas-liquid mass transfer and to interpret the change of $C_D$. To date, most of the previous works put their emphasis on dealing with mass transfer coefficient in spray towers. Turpin et al. [15,16], Javed et al. [17], Codolo et al. [18,19], Yeh and Rochelle [20], Dimiccoli et al. [21], Tanda et al. [22], Ma et al. [23], and Zeng et al. [24] had experimentally determined mass transfer coefficients and founded empirical correlations. According to these literatures, the mass transfer coefficient in our work can be calculated by the following relation:

$$\frac{1}{K_g} = \frac{1}{k_{g,a}} + \frac{1}{EHk_l}.$$  \hspace{1cm} (4)
In the experiment, the neutralization between H$_2$S and Na$_2$CO$_3$ was rapid and it was considered to be pseudo-first-order. Thus the overall mass transfer coefficient can be described in terms of individual mass transfer coefficients. Based on the two-film theory, considering that there is an excess of Na$_2$CO$_3$ concentration, the reactant in the liquid film does not decrease throughout the spraying process. Although H$_2$S is sparingly soluble, a fast chemical reaction consisted of an enhancement factor (E) promoting the solubility coefficient (H) of H$_2$S in water [15]. In this case, the mass transfer rate is controlled by the gas phase resistance, and the liquid phase resistance can be ignored, so

$$K_g \equiv k_g.$$  \hspace{1cm} \text{(5)}

According to Codolo et al. [19], the gas phase volumetric mass transfer coefficient ($k_g a$) can be calculated by equation:

$$k_g a = \frac{Q_G}{AhRT} \ln \left( \frac{C_{H_2S,I}}{C_{H_2S,D}} \right), \hspace{1cm} \text{(6)}$$

where $a$ is the volumetric interfacial area, $Q_G$ is the gas flow rate, $A$ is the area of the column, $h$ is the distance between sampling ports and the bottom of column, $R$ is the universal gas constant, $T$ is the temperature (25°C), $C_{H_2S,I}$ is the inlet concentration of H$_2$S, and $C_{H_2S,D}$ is the dilution concentration of H$_2$S measured in 120 seconds.

Figure 4 illustrates the variations of $k_g a$ for H$_2$S absorption under different experimental conditions. As seen, $k_g a$...
increased in all of the four tests. It is well known that an increase of $k_ga$ was conducive to the $H_2S$ absorption and the reduction of $C_D$, but it was reversed with the results in Figures 4(a) and 4(b). This was because an improvement of $k_ga$ was implemented by increasing the numbers of $H_2S$ molecules, and the interpretation could be demonstrated with the formula of $H_2S$ removal efficiency proposed by Turpin et al. [15]. It revealed that $H_2S$ absorption effectiveness was inversely proportional to $C_{H_2S,I}$ and $Q_G$ although $k_ga$ increased with gaseous concentrations and gas release rates. On the other side, the results of $k_ga$ in Figures 4(c) and 4(d) show a good coincidence with absorption effectiveness. Indeed, when $C_{Na_2CO_3}$ increased, more $Na_2CO_3$ molecules diffused into the gas-liquid interface, liquid phase mass transfer resistance ($1/\varepsilon H_k_o$) decreased, and so $k_ga$ was improved. When $Q_L$ increased, the larger numbers of droplets available for the transfer led to the increase of $k_ga$. Evidently, these two actions both promoted $H_2S$ absorption while keeping $H_2S$ releases constant.

Combined with Sections 3.2.1 and 3.2.2, it is easily observed that water sprays express eligible performance for $H_2S$ release control even though their dilution capacity was weakened at high gaseous concentrations and rates of releases. The presence of $Na_2CO_3$ can significantly improve the absorption of $H_2S$ in water with only decreasing $C_D$ and the optimal $Na_2CO_3$ additive was found to be 1.0 g.L$^{-1}$ in this test. Compared with $Na_2CO_3$, adjusting water flow rate may be an effective strategy in enhancing dilution capacity of water sprays due to the fact that larger flow rate led to both less $T_D$ and $C_D$. Perceptibly, unlike a small scope of $C_D$ between 1.4 and 4.5 ppm, $T_D$ varied at a broad range of 50 to 90 seconds. This illustrates that internal and extrinsic parameters had more profound impact on the dilution rate than the absorption effectiveness of water sprays, suggesting that the movement of air flow played a significant role in the dispersion of gas releases. As a result, a promising future can be expected with intensive studies on the reduction of dilution rate.

3.3. The Improvement of Using Multinozzle Configuration for the Dilution Capacity of Water Sprays. As mentioned
above, increasing the water flow rate was the most effective migration pathway for the accidental releases of H$_2$S gas. Unfortunately, as more water is reserved and consumed, the cost-per-use of water spray would rise during use. To reduce the water consumption without undermining the dilution capacity, some tests with comparisons between one-nozzle set and four-nozzle set were performed in case of the same total water consumption. Simultaneously, different opening angles were produced to keep the similar coverage area of the volume in the column by droplets, as illustrated in Figure 5; the advantage of this design was able to eliminate the wall effects in gas detection.

Figure 6 compares the dilution capacity of water sprays using two spray nozzle configurations. It can be observed that, in light of $T_D$ and $C_D$, the effectiveness of using four-nozzle set was better in the water flow rate range of $1.6 - 6.7 \times 10^{-5} \text{m}^3\text{s}^{-1}$. This can be explained by the different droplet sizes dependent on the nozzles. In the processes of spraying, the droplets provided affluent interfacial area through which the gas-liquid mass transfer took place [15]. Because of breakup and coalescence mechanisms, the droplets generated by a given nozzle do not have the same size after their formation but at best belong to the same range of sizes. Previous studies [16, 21] have demonstrated the distribution of droplet size was Gaussian, and it was narrower with nozzles which had a smaller orifice diameter. As for spray nozzles, their orifice diameters are always special and must be matched with $Q_L$ [18]. For a fixed liquid flow rate, when four small nozzles were used together, the size of droplet became smaller with the increasing number of droplets, and so the exchange area available for the gas-liquid transfer got bigger. The increasing number of droplets did not only enhance the air flow, but also improve the gas-liquid mass transfer. In fact, the use of multinozzle set did very well both in water consumption and in performance improvement. Moreover, this means could also significantly reduce the impact of using alkaline additive on the earth’s surface.

4. Conclusions

This study demonstrated that accidental releases of hazardous H$_2$S gas can be well controlled by utilizing water sprays with the presence of alkaline additives. Water sprays express eligible performance for H$_2$S release control even though their dilution capacity was weakened at high gaseous concentrations and rates of releases. The presence of Na$_2$CO$_3$ can significantly improve the absorption of H$_2$S in water and the optimal Na$_2$CO$_3$ additive was found to be 1.0 g L$^{-1}$. Adjusting water flow rates is preferable to enhance dilution capacity of water sprays because of the fact that larger flow rate led to both less $T_D$ and $C_D$. Furthermore, the dilution rate or $T_D$ is more greatly impacted by internal and extrinsic condition, implying that strengthening the interference of air flow was a preferable strategy in the dispersion of gas releases. For the nozzle configurations test, the results illustrated using multinozzle set poses advantages in the water conservation and the improvement of dilution capacity. This study, to some extent, fills the gap of reducing the hazard caused by releases of H$_2$S that few researches have focused on previously.

Nomenclature

Roman Symbols

$A$: Area of the spray tower (m$^2$)
$a$: Volumetric interfacial area (m$^2$$\cdot$ m$^{-3}$)
Greek Symbols

\(\tau\): Viscous forces of gas flow (Pa)

\(\rho\): Gas density (Kg m\(^{-3}\))

\(\mu\): Gas viscosity (Pa·s).

Subscript

\(I\): Inlet

\(D\): Dilution.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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