Hydrogen sulfide generation suppression by nitrate addition – application to solid waste landfill site

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Abstract: In Japan, three deaths were reported at an inert solid waste landfill site after exposure to hydrogen sulfide (H2S) generated at the site. H2S gas is produced when sulfate-reducing bacteria (SRB) convert sulfate derived from waste gypsum board under anaerobic conditions. The recommended countermeasure is to supply oxygen by installing gas venting pipes. However, a large cost is necessary for pipe installation and the pipes are not applicable to coastal landfill sites. On the other hand, H2S generation suppression by nitrate (NO3) addition has been reported in sewage systems. In this study, in order to develop a method to suppress H2S generation by NO3 addition at a landfill site, the extent of suppression was quantitatively estimated.

When NO3 reagent was added at the rate of 0.46 mmol-NO3/(L·d) into a liquid from which H2S gas was generated at the rate of 0.21 ± 0.05 mmol-H2S/(L·d), H2S generation rate was decreased to approximately 1/4 of the original rate. Although it was difficult to maintain the concentration of NO3 because it tended to disappear rapidly, the frequent addition of NO3 reagent to maintain the concentration of approximately 430 mg-NO3/L enabled us to control H2S concentration to below 1000 ppmv for one month and H2S generation rate to below 1/20 of the original rate.

Keywords: Landfill Site, Waste Gypsum Board, Hydrogen Sulfide, Generation Suppression, Nitrate

1. Introduction

A strong offensive smell likened to rotten egg odor is recognizable when hydrogen sulfide (H2S) gas is present in air at 20–30 ppmv (v: volume) [1]. Inhalation of H2S gas at 750–1000 ppmv causes abrupt physical collapse [2] (hereafter, H2S exceeding 1000 ppmv is called H2S high). H2S gas is generated at landfill sites globally [3–8]. In 1999, three workers at an inert solid waste landfill site (a type of landfill site in Japan where waste plastic, rubber, metal, glass, ceramic, and construction and demolition debris (stones, bricks, and blocks) are acceptable, as well as waste gypsum board without protective paper sheet at the time of the accident. No gas venting pipes, liner for leachate, or water treatment facility was available,) died of exposure to 15000 ppmv H2S gas. H2S gas is produced at a landfill when sulfate-reducing bacteria (SRB) consume organic matter and convert sulfate under anaerobic conditions [3, 9, 10]. The source of sulfate in construction and demolition debris is predominantly gypsum (CaSO4) [11]. No biodegradable organic matter is acceptable at inert solid waste landfill sites in Japan. Therefore, only waste gypsum board from which protective paper sheet had been removed could be disposed at those landfill sites. Following the report that organic matter in waste gypsum board base material (gypsum part) showed potential for H2S generation [12], the Ministry of the Environment in Japan issued a notice prohibiting the disposal of waste gypsum board at inert solid waste landfill sites in 2006 (Notice: Treatment of waste gypsum board from which protective paper sheet had been removed). Suggested measures for preventing H2S generation or diffusion at a landfill site include the exclusion of anaerobic conditions (water exclusion and/or oxygen supply) [13], trapping of generated H2S gas (conversion into iron sulfide using material containing iron [14, 15], and adsorption by activated carbon [16] or zeolite [17]). The Ministry of the Environment in Japan recommended the appropriate installation of cover soil (to prevent rainwater percolation and trap H2S gas
generated by iron in soil) and the use of gas venting pipes (oxygen supply). However, in regard to the gas venting pipe, a large cost is necessary for installation and the identification of \( \text{H}_2\text{S} \) generation spots as the installation points. In addition, oxygen supply to the waste layer via gas venting pipes is impossible at coastal landfill sites because a major portion of the waste layer is found below the surface of inner leachate. Trapping by iron does not prevent \( \text{H}_2\text{S} \) generation per se. Therefore, it is necessary to develop a method to suppress \( \text{H}_2\text{S} \) generation.

In sewage systems, \( \text{H}_2\text{S} \) generation suppression by nitrate (\( \text{NO}_3^− \)) addition has been reported \([18, 19]\). This was attributed to the increase in oxidation-reduction potential (ORP) caused by the presence of \( \text{NO}_3^− \). As Gibbs free energies of oxidation of organic matter (\( \text{CH}_3\text{O} \)) with dissolved \( \text{O}_2 \), \( \text{NO}_3^− \), and sulfate (\( \text{SO}_4^− \)) as the electron acceptor were \(-125, -119\), and \(-25.4 \text{ kJ/mol} \) \([20]\), respectively, the reaction occurred in the order of respiration by aerobic bacteria > denitrification by denitrifying bacteria > \( \text{SO}_4^− \) reduction by SRB (\( \text{H}_2\text{S} \) generation) \([20]\). Therefore, if dissolved \( \text{O}_2 \) or \( \text{NO}_3^− \) exists, \( \text{SO}_4^− \) reduction hardly occurs.

If the \( \text{NO}_3^− \) addition method were applicable to the waste layer as well, that method would be a realistic \( \text{H}_2\text{S} \) generation suppression method at an actual landfill site. However, no quantitative investigation has been undertaken, such as the determination of the amount of \( \text{NO}_3^− \) required to suppress \( \text{H}_2\text{S} \) generation. \( \text{NO}_3^− \) reagent is used in sewage systems \([19]\). Compost made from waste organic matter also contains \( \text{NO}_3^− \) \([21, 22]\). Therefore, if useless \( \text{NO}_3^− \) in the market could be used at landfill sites, low cost and effective use of resources would be accomplished.

In this study, in order to develop a method for suppressing \( \text{H}_2\text{S} \) generation by \( \text{NO}_3^− \) addition at a landfill site, the following parameters were quantitatively estimated.

- Concentration of \( \text{NO}_3^− \)
- \( \text{NO}_3^− \) addition method (intermittent addition and concentration maintenance)
- \( \text{NO}_3^− \) type (reagent and compost)

2. Materials and Methods

2.1. Outline of Experiments

2.2. Materials

Table 1. Details of samples.

<table>
<thead>
<tr>
<th>Component</th>
<th>Product name, company</th>
<th>Amount used for a ( \text{H}_2\text{S} ) generation bottle</th>
</tr>
</thead>
<tbody>
<tr>
<td>Organic matter</td>
<td>Dried Yeast Extract D-3, Wako Pure Chemical Industries</td>
<td>700 ~ 1000 mg-C/L</td>
</tr>
<tr>
<td></td>
<td>Lactose Broth DAIGO, Wako Pure Chemical Industries (equivalently mixed, and added into pure water)</td>
<td>25 g</td>
</tr>
<tr>
<td>Calcium Sulfate</td>
<td>Calcium Sulfate (( \text{CaSO}_4·2\text{H}_2\text{O} )), Japanese Food Additives, Wako Pure Chemical Industries</td>
<td>750 mg/L</td>
</tr>
<tr>
<td>Nutrient</td>
<td>BOD Nutrient Buffer Pillows for 6 L sample, APHA Formulation, HACH COMPANY (1 pillow mixed with 500 mL pure water)</td>
<td>25 mL</td>
</tr>
<tr>
<td>Silica sand</td>
<td>TOYOURA KEISEKI KOGYO</td>
<td>25 g</td>
</tr>
<tr>
<td>Seeding</td>
<td>Black sediment in an ornamental pond (5 g mixed with 500 mL pure water)</td>
<td>25 mL</td>
</tr>
<tr>
<td>Nitrate (reagent)</td>
<td>Sodium Nitrate, 1st grade, Wako Pure Chemical Industries</td>
<td>Depending on the condition</td>
</tr>
<tr>
<td>Nitrate (compost)</td>
<td>Sewage sludge compost</td>
<td></td>
</tr>
</tbody>
</table>

As only basic experiments were performed in this study, no actual sample, i.e., leachate from landfill site, was used. Medium for microbial culture and calcium sulfate (\( \text{CaSO}_4·2\text{H}_2\text{O} \)) were used as organic matter and \( \text{SO}_4^− \) sources,

In this study, \( \text{H}_2\text{S} \) gas was generated in an airtight bottle, and the effect of \( \text{H}_2\text{S} \) generation suppression by \( \text{NO}_3^− \) addition was evaluated. Specifically, organic matter and \( \text{SO}_4^− \) were introduced into the bottle, and an anaerobic condition was preserved. Then, the reproducibility of \( \text{H}_2\text{S} \) generation was confirmed. \( \text{H}_2\text{S} \) in liquid and gas phases was removed by bubbling nitrogen (\( \text{N}_2 \)) gas, \( \text{NO}_3^− \) was added into the bottle, and the duration of \( \text{H}_2\text{S} \) generation suppression and the \( \text{H}_2\text{S} \) re-generation rate were measured. Sodium nitrate (\( \text{NaNO}_3 \)) reagent and extract from sewage sludge compost were used as \( \text{NO}_3^− \) sources. Two methods of \( \text{NO}_3^− \) addition were adopted: intermittent addition and concentration maintenance (Fig. 1).

Figure 1. Outline of intermittent addition (a) and concentration maintenance (b) test.
respectively. NaNO₃ reagent and extract from sewage sludge compost were used as NO₃ sources. Hereafter, reagent NO₃ and NO₃ in extract from compost were represented by Nₐ and NₐC, respectively. Sewage sludge compost and water were mixed at the weight ratio of 1:8 and stirred well, and the supernatant was collected as extract. The concentrations of NO₃ and total organic carbon (TOC) in the supernatant were approximately 3500 mg-NO₃/L and 1900 mg-C/L, respectively. Details of the samples are shown in Table 1.

2.3. Experimental Setup

As shown in Fig. 2, an airtight bottle was made by connecting a gas washing bottle (polycarbonate and polyethylene) to a gas sampling bag (vinylidene fluoride) to a gas sampling bag (vinylidene fluoride) connecting a gas washing bottle (polycarbonate and polyethylene) to a gas sampling bag (vinylidene fluoride) to a gas sampling bag (vinylidene fluoride) to a gas sampling bag (vinylidene fluoride). The gas sampling bag was filled with N₂ gas. Samples were introduced into the bottle in the amounts shown in Table 1, and pure water was added to make 350 mL. Total gas volume of head in the bottle and the gas sampling bag was approximately 700 mL.

2.4. Experimental Methods for Acclimation

The bottle conditions for H₂S high generation were as follows: maintenance of (1) appropriate environment for multiplication of SRB (anaerobic condition, temperature for mesophilic bacterial growth), (2) high concentration of organic matter, and (3) presence of SO₄ [12]. To maintain condition (1), oxygen absorbent (tube filled with sodium sulfite solution) was introduced into the H₂S generation bottle, and the bottle was set in an incubator (35 °C). To maintain condition (2), TOC in the liquid phase was measured two times a week, organic matter was injected, and TOC after the injection was re-measured. Thus, TOC was maintained in an amount ranging from 700 to 1000 mg-C/L.

To maintain condition (3), SO₄ was introduced into the bottle in an amount equivalent to 30 times that required for the saturation of CaSO₄·2H₂O (approximately 1700 mg-SO₄/L, 17.6 mmol-SO₄/L [23]).

Nine H₂S generation bottles (RUNS 1–9) were prepared. H₂S in the liquid and gas phases was removed by bubbling N₂ gas when H₂Shigh was observed. H₂S high observation and H₂S removal were conducted three times as the acclimation stage, and then, the H₂S generation suppression test was performed.

2.5. Experimental Methods for H₂S Generation Suppression

In the H₂S generation suppression test, NO₃ was added into the H₂S generation bottle after acclimation was completed, and its effect on H₂S generation was evaluated. High (H) and low (L) concentrations of NO₃ were added, i.e., 7.0 mmol-NO₃/L (430 mg-NO₃/L) and 1.76 mmol-NO₃/L (110 mg-NO₃/L), respectively. Those concentrations are 0.4 and 0.1 times the saturation concentration of SO₄ (17.6 mmol-SO₄/L).

Although ideally, the experiments should be conducted in individual bottles, because of limited space and budget, the same bottle (as it is, no changes of content) was used repeatedly for the experiments. After the intermittent addition test (I), the concentration maintenance test (M) was conducted in RUNS 1–6. Control experiments (no NO₃ addition) were performed in RUNS 7–9.

The procedures and the end conditions for each experiment are as follows. In the intermittent addition test, HNₐL or HNₐC was added into the bottle and conditions (1)–(3) were maintained. When the H₂S generation suppression effect of NO₃ disappeared and H₂S high was observed, H₂S was removed by bubbling N₂ gas, and NO₃ was added again. The experiment was terminated after observing H₂S high six times. In the concentration maintenance test, conditions (1)–(3) were maintained, and HNₐ or HNₐC was added into the bottle to maintain NO₃ concentration from 100 to 430 mg-NO₃/L. The experiment was terminated when H₂S concentration could be controlled to below 1000 ppmv for one month.

The experimental conditions and procedures are shown in Table 2. The abbreviations of the experiments are also listed in Table 2. For example, the abbreviation for high concentration (H), reagent NO₃ (Nₐ), and intermittent addition test (I) is HNₐI.

<table>
<thead>
<tr>
<th>Experiment type</th>
<th>Abbreviation</th>
<th>Procedure</th>
<th>NO₃ addition (mg-NO₃/L)</th>
<th>End condition</th>
<th>RUN No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acclimation</td>
<td>Nₐ</td>
<td>*—H₂S₀ high generation—H₂S removal—back to *</td>
<td>0</td>
<td>3 times of H₂S₀ high generation</td>
<td>1—9</td>
</tr>
<tr>
<td>High conc. nitrate (reagent)</td>
<td>HNₐI</td>
<td>*—H₂S₀ high generation—H₂S removal—HNₐ addition—back to *</td>
<td>430</td>
<td>6 times of H₂S₀ high generation</td>
<td>1, 2, 3</td>
</tr>
<tr>
<td>Intermittent addition</td>
<td>LNₐI</td>
<td>*—H₂S₀ high generation—H₂S removal—LNₐ addition—back to *</td>
<td>110</td>
<td>6 times of H₂S₀ high generation</td>
<td>4, 5, 6</td>
</tr>
</tbody>
</table>
2.6. Analytical Procedure

The objects of measurement were the gas and liquid phases in the H$_2$S generation bottle. Measurement items for the gas phase were H$_2$S concentration and gas volume. Measurement items for the liquid phase were pH, electric conductivity (EC), ORP, TOC, NO$_3$ concentration, and liquid volume.

In regard to the gas phase, H$_2$S was measured with a portable gas detector for worker safety (XS-2200, controlled potential electrolysis, NEW COSMOS ELECTRIC CO., LTD.). Gas volume in the gas bag was measured by reading the scale on a plastic syringe used to withdraw the gas from the bag. Then, the gas bag was newly filled with N$_2$ gas and reconnected to the bottle.

In regard to the liquid phase, HORIBA B-212 (pH), HORIBA B-173 (EC), HORIBA-D-55 and 9300-10D (ORP), Shimadzu TOC-V (TOC), and HORIBA B-343 (NO$_3$) were used. Liquid volume was estimated by measuring the gross weight of the H$_2$S generation bottle. Liquid (10 mL) was sampled from the liquid sampling port (Fig. 2) with a plastic syringe. Liquid volume in the H$_2$S generation bottle was maintained by adding 10 mL solution containing organic matter or NO$_3$.

H$_2$S gas volume, pH, EC, ORP, and NO$_3$ concentration were measured four times a week, and TOC was measured two times a week. In addition, TOC was re-measured immediately after adding organic matter.

3. Results

Changes in the concentrations of H$_2$S and NO$_3$, and the ORP in RUNS 1, 4, and 7 are shown in Fig. 3, 4, and 5, respectively. The results of RUNS 2, 3, 5, 6, 8, and 9 are omitted. The pH ranged from 5.9 to 8.8, was increased with time, and was around 8 after 30 days. EC ranged from 3.2 to 11.9 mS/cm and was increased with time upon the addition of NO$_3$.

3.1. Intermittent Addition Test

ORP in HN$_3$I was increased upon the addition of NO$_3$. On the other hand, ORP in LHN$_3$I and HN$_3$I did not show a constant increase. H$_2$S$_{high}$ was generated when ORP was below −100 mV (standard hydrogen electrode). Regarding HN$_3$I and HN$_3$C, there were cases that NO$_3$ concentration was decreased to below the detection limit (50 mg-NO$_3$/L) on the next measurement day, i.e., after two days. Therefore, NO$_3$ might have disappeared in two days.

3.2. Concentration Maintenance Test

Because of the rapid disappearance of NO$_3$ in HN$_3$M, NO$_3$ reagent had to be added frequently. NO$_3$ concentration could not be maintained at an exact value because it was below the detection limit when NO$_3$ reagent was added. ORP was increased and exceeded 100 mV with the repeated addition of NO$_3$ reagent. H$_2$S$_{high}$ was not generated for one month, i.e., the target time. Although NO$_3$ concentration was decreased slowly and NO$_3$ was added only two times in HN$_3$M, H$_2$S$_{high}$ was not generated for one month. ORP was below −100 mV.

3.3. Control

ORP was below −100 mV after 10 days and H$_2$S$_{high}$ was generated repeatedly in control (Fig. 5). ORP exhibited both increases and decreases, and no obvious tendency was observed. The regeneration of H$_2$S immediately after H$_2$S removal by bubbling N$_2$ gas was slower than that immediately before removal. NO$_3$ concentration was near the detection limit.

![Figure 3. Concentration changes in RUN 1.](image-url)
4. Discussion

4.1. Quantitative Evaluation of H$_2$S Generation Suppression by NO$_3$ Addition

The effect of NO$_3$ addition on H$_2$S generation suppression was quantitatively estimated as follows. The number of days required for exceeding 1000 ppmv H$_2$S is shown in Fig. 6. In control, 7.6 ± 2.1 days (average ± standard deviation) were required for exceeding 1000 ppmv H$_2$S. The required number of days in LN$_R$I and HN$_C$I was almost the same as that in control. On the other hand, in the case of HN$_R$I, 15.2 ± 8.2 days were required, i.e., twice that of control in spite of the large variance. H$_2$S$_{high}$ was not generated in HN$_R$M and HN$_C$M for one month.

H$_2$S generation rates are shown in Fig. 7. Generation rate was determined from the increase of H$_2$S concentration per unit time from the day of H$_2$S removal by bubbling N$_2$ gas to the day H$_2$S exceeded 1000 ppmv (However, two days were used for the concentration maintenance test). It is known that H$_2$S exists in not only the gas phase but also the liquid phase. Using the concentration in the gas phase, gas volume, liquid volume, and pH, concentration in the liquid phase was calculated according to Henry's law and an equilibrium relationship in the liquid phase [24]. As H$_2$S was generated from the liquid phase, the generation rate was converted into the rate per unit liquid volume (mmol-H$_2$S/(L·d)). The generation rate in control was 0.21 ± 0.05 mmol-H$_2$S/(L·d). The rates in LN$_R$I and HN$_C$I were the same as that in control. On the other hand, the rate in HN$_R$I was 0.051 ± 0.024 mmol-H$_2$S/(L·d), i.e., approximately 1/4 of control. In spite of the disappearance of NO$_3$, H$_2$S was not generated immediately, i.e., the generation was suppressed from 60 to 80 days. The reason for the lack of decrease of the generation rate in HN$_R$I is unknown. The rates in the concentration maintenance test (HN$_R$M and HN$_C$M) were below 1/20 of control. However, NO$_3$ concentration could not be maintained because of its rapid disappearance in HN$_R$M.

NO$_3$ addition rates are shown in Fig. 8. The rates in LN$_R$I, LN$_N$I, HN$_R$I, and HN$_C$I ranged from 0.20 to 0.71 mmol-NO$_3$/L·d), whereas that in HN$_R$M was more than 3-fold, i.e., 2.2 mmol-NO$_3$/L·d). This is because the experimental conditions required that NO$_3$ concentration be maintained at 100 to 430 mg-NO$_3$/L, i.e., it was not our purpose to determine the minimum concentration of NO$_3$ required to suppress H$_2$S$_{high}$ generation. In addition, NO$_3$ disappeared rapidly. Therefore, it is possible to suppress

![Figure 4. Concentration changes in RUN 4.](image1)

![Figure 5. Concentration changes in RUN 7 (control).](image2)

![Figure 6. Number of days required for exceeding 1000 ppmv H$_2$S.](image3)

Figure 4. Concentration changes in RUN 4.

Figure 5. Concentration changes in RUN 7 (control).

Figure 6. Number of days required for exceeding 1000 ppmv H$_2$S.
H₂S generation even if the NO₃ addition rate is below 2.2 mmol-NO₃/(L·d). For example, if HN₄I was regarded as having H₂S generation suppression effect because of the decreased H₂S generation rate, H₂S generation was possibly suppressed by the above NO₃ addition rate of 0.46 mmol-NO₃/(L·d) in HN₄I.

Regarding the addition of NO₃ derived from compost, it was assumed that the frequent addition of NO₃ in HN₄M was required because of the rapid disappearance of NO₃, in the same manner as that in HN₄M. However, the results (Fig. 3) indicated that the decrease of NO₃ concentration was slow in HN₄M, and H₂S generation was suppressed by the addition of NO₃ in small amounts. In addition, the disappearance of NO₃ proceeded more slowly in HN₄M than in HN₄I in spite of use of the same NO₃ derived from compost (Fig. 4). The internal environment might have been changed because some experiments were continuously conducted in the same bottle after another experiment was completed. Compost contains stable organic matter, such as humic substances [25]. A larger amount of stable organic matter was contained in compost made from sewage sludge than in compost made from food waste [26]. The hydrophobic domains in humic substances prevent microbial activity associated with water [27]. In this study, medium for microbial culture was added as organic matter to maintain TOC at 700–1000 mg-C/L. However, when extract from compost was used for NO₃ addition, humic substances contained in compost would be included as well. As humic substances are also organic matter, they would increase TOC in the bottle and consequently decrease the amount of organic matter derived from medium for microbial culture. Thus, the authors speculate that H₂S generation potential was decreased in HN₄M because TOC derived from humic substances, which are stable organic matter, was increased and consequently, the net amount of TOC available to SRB was decreased. This result led to two suggestions: the H₂S generation suppression effect in HN₄M was overestimated, and H₂S generation potential did not increase in spite of the increase of TOC due to humic substances contained in compost (availability of use at an actual landfill site).

The amount of NO₃ to be added to a waste layer of a landfill site where H₂S is generated can be estimated from the results obtained in this study. Future issues are as follows. In regard to the experiment using NO₃ derived from compost, additional experiments are required with control of the net amount of organic matter. Environmental loading, such as eutrophication by application of the NO₃ addition method at a pilot scale or an actual landfill site, and cost reduction by using useless NO₃ in the market should be evaluated. As NO₃ addition is an alternative method for supplying oxygen, its advantages should be evaluated quantitatively. The advantages include no consumption of large amounts of NO₃.
in the aerobic zone and consumption of organic matter by denitrification. Specifically, the decomposition of organic matter has to rely on anaerobic decomposition because oxygen supply via gas venting pipes to the waste layer at a coastal landfill site, which has a large amount of retained inner leachate, is not feasible. If both H$_2$S generation suppression and the consumption of large amounts of organic matter by denitrification could be realized, stabilization of waste layer at landfill site would be accelerated.

5. Conclusion

In this study, in order to develop a method to suppress H$_2$S generation by NO$_3$ addition at a landfill site, the extent of suppression was quantitatively estimated. When NO$_3$ reagent was added at the rate of 0.46 mmol-NO$_3$/L·d into a liquid from which H$_2$S gas was generated at the rate of 0.21 ± 0.05 mmol-H$_2$S/L·d, H$_2$S generation rate was decreased to approximately 1/4 of the original rate. Although it was difficult to maintain the concentration of NO$_3$ because of its rapid disappearance, by frequently adding NO$_3$ to maintain a concentration of approximately 430 mg-NO$_3$/L, the concentration of H$_2$S would be controlled to below 1000 ppmv for one month and H$_2$S generation rate would be reduced to below 1/20 of the original rate. The disappearance of NO$_3$ derived from compost was slow and H$_2$S generation was suppressed by the addition of a small amount of NO$_3$. Additional experiments are required as the net amount of organic matter for SRB could not be controlled.

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References


