Suppressing Hydrogen Sulfide Generation by Nitrate or Oxygen Addition in Column Percolation Experiment

Shumpei Kitazaki[1], Kei Nakagawa[1], Tomonori Kindaichi[2], Hiroshi Asakura[1, *]

[1]Graduate School of Fisheries Science and Environmental Studies, Nagasaki University, Nagasaki, Japan
[2]Graduate School of Engineering, Hiroshima University, Hiroshima University, Higashihiroshima, Japan

Email address:
asakura_hiroshi@yahoo.co.jp (H. Asakura)

Abstract: H_2S generation suppression by the addition of NO_3 from reagent (NR) or compost (NC), and O_2 supply (OX) was quantitatively estimated in column percolation experiments. The cumulative amounts of oxygen added exceeded 300 mmol-O/L in NR and NC, and approximately 2 mmol-O/L in OX on day 75. The cumulative amounts of H_2S generated on day 60 in control, NR, NC, and OX were 69, 26, 71, and 31 mmol-H_2S/L, respectively. The amounts in NR and OX were half of that in control, whereas the amount in NC was almost the same as that in control. The H_2S generation rates from day 50 to day 60 in control, NR, NC, and OX were 0.86, 0.019, 0.75, and 0.041 mmol-H_2S/(L·d), respectively, and the rates in NR, NC, and OX were 0.02, 0.9, and 0.05 times that in control. In this way, the H_2S generation suppression effects of NO_3 reagent addition were observed. In NR, although NO_3 was injected from the top of the column, the suppression effect reached the deep layer.

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

1. Introduction

Hydrogen sulfide (H_2S) gas is generated at landfill sites globally [1–6]. The inhalation of H_2S gas at 750–1000 ppm causes abrupt physical collapse [7] (hereafter, H_2S exceeding 1000 ppm is called H_2S_{high}). 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 are acceptable, as well as waste gypsum board without protective paper sheet at the time of the accident. No gas venting pipes are required.) died of exposure to 15000 ppm H_2S gas. H_2S gas is produced at a landfill when sulfate-reducing bacteria (SRB) consume organic matter and convert sulfate (SO_4) under anaerobic conditions [1, 8, 9]. The source of SO_4 in construction and demolition debris is predominantly gypsum ($CaSO_4$) [10]. Suggested measures for preventing H_2S generation or diffusion at a landfill site include the exclusion of anaerobic conditions (by water exclusion and/or oxygen (O_2) supply) [11], and the trapping of generated H_2S gas (by conversion into iron sulfide using iron-containing material [12, 13], and by adsorption to activated carbon [14] or zeolite [15]). The Ministry of the Environment in Japan recommended the appropriate installation of cover soil (to

prevent rainwater percolation and trap generated H_2S gas by iron in soil) and the use of gas venting pipes (O_2 supply). However, in regard to the gas venting pipe, a large cost is necessary for the installation and the identification of H_2S generation spots as the installation points. In addition, oxygen supply to the waste layer via gas venting pipes is not possible at coastal landfill sites because a major portion of the waste layer is found below the surface of inner leachate. It is also a fact that trapping by iron does not prevent H_2S generation per se. Therefore, it is necessary to develop a method to suppress H_2S generation.

In sewage systems, H_2S generation suppression by nitrate (NO_3) addition has been reported [16, 17]. This has been attributed to the increase in the oxidation-reduction potential (ORP) caused by the presence of NO_3. As the Gibbs free energies of the oxidation of organic matter (CH_2O) with dissolved O_2, NO_3, and sulfate (SO_4) as the electron acceptor are −125, −119, and −25.4 kJ/mol [18], respectively, the reaction is said to occur in the order of respiration by aerobic bacteria > denitrification by denitrifying bacteria > SO_4 reduction by SRB (H_2S generation) [18]. Therefore, if

dissolved O_2 or NO_3 exists, SO_4 reduction hardly occurs.

If the NO_3 addition method were applicable to the waste layer as well, that method would be a realistic H_2S generation suppression method at an actual landfill site. NO_3 reagent is used in sewage systems [17]. Compost made from waste organic matter also contains NO_3 [19, 20]. Therefore, if useless NO_3 in the market could be used at landfill sites, low cost and effective use of resources would be accomplished.

The authors quantitatively estimated H_2S generation suppression by NO_3 (reagent and compost-derived) addition [21]. The experiment was conducted on a beaker scale and in a complete mixing system. However, column percolation experiments are required to study the applicability of the NO_3 addition method at an actual landfill site. In regard to the addition of compost-derived NO_3, not only the injection of extract derived from compost into the waste layer, but also the utilization of rainfall infiltration through compost on top of the waste layer is assumed. Furthermore, as NO_3 addition is an alternative method for supplying oxygen, H_2S generation suppression by NO_3 addition should be compared with that by O_2 supply.

In this study, H_2S generation suppression by the addition of NO_3 from reagent and compost, and O_2 supply was quantitatively estimated by conducting column percolation experiments.

2. Materials and Methods

2.1. Outline of Experiments

H_2S was generated in an airtight acrylic column, and H_2S generation suppression by NO_3 or O_2 addition was evaluated. Specifically, the column was filled with gypsum, organic matter solution was introduced from the top, and an anaerobic condition was preserved. Then, the reproducibility of H_2S_{high} generation was confirmed. H_2S in liquid and gas phases was removed by bubbling nitrogen (N_2) gas. NO_3 or O_2 was added into the column, and the concentration of re-generated H_2S was measured.

2.2. Materials

Table 1. Details of samples.

Component	Product name, company, type
Organic matter	Dried Yeast Extract D-3, Wako Pure Chemical Industries Lactose Broth DAIGO, Wako Pure Chemical Industries (equivalently mixed)
SO_4	Waste gypsum board (crushed into <10 mm particles)
Gravel	<10 mm, washed with water
Nutrient	BOD Nutrient Buffer Pillows for 6 L sample, APHA Formulation, HACH COMPANY (1 pillow mixed with 500 mL pure water)
Seeding	Black sediment in an ornamental pond (3 g mixed with 500 mL pure water)
NO_3 (reagent)	Sodium Nitrate, 1st grade, Wako Pure Chemical Industries
NO_3 (compost)	Sewage sludge compost
O_2	Aerated water or air bubbling

Details of the samples are shown in Table 1. Medium for microbial culture and waste gypsum board ($CaSO_4 \cdot 2H_2O$) were used as sources of organic matter and SO_4, respectively. Sodium nitrate ($NaNO_3$) reagent and sewage sludge compost were used as sources of NO_3, and air was used as the source of O_2. NO_3 content in the compost was 2.8 g-NO_3/100 g-compost.

2.3. Experimental Setup

As shown in Figure 1, an airtight column was made by connecting the acrylic column (10 cm inner diameter, 40 cm height, and 3.1 L inner volume) to a 100 mL plastic syringe. The syringe was filled with 50 mL of N_2 gas. The column was filled with solid sample (1.8 kg of a mixture of gypsum particles and gravel in 1:10 weight ratio; called waste layer hereafter). The height of the waste layer was 35 cm. Then, 400 mL of a mixture of nutrient and seeding was added. Tap water was introduced to a height of 30 cm. Four columns were prepared, i.e., columns for control, NO_3 (reagent) addition, NO_3 (compost) addition, and O_2 addition. Hereafter, those columns are called control, NR, NC, and OX, respectively.
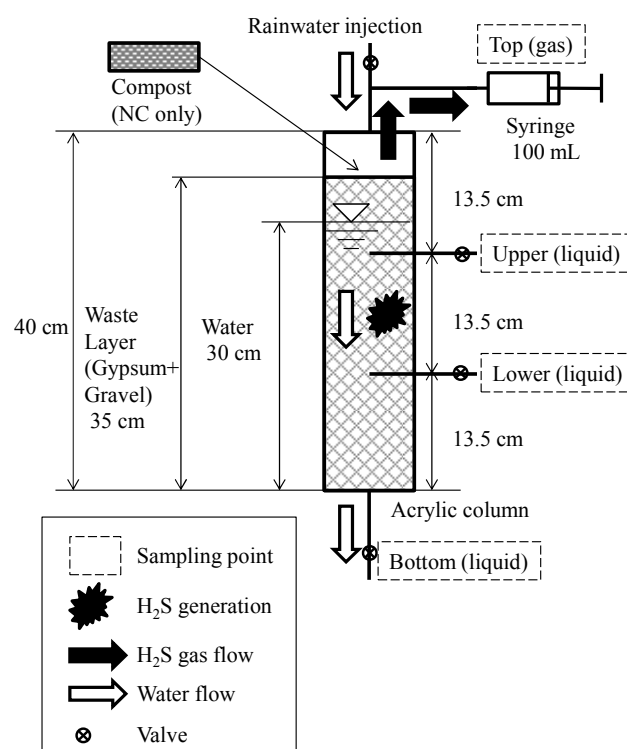

Figure 1. Schematic diagram of column.

2.4. Experimental Methods

At first, the stable generation of H_2S_{high} is necessary prior to the H_2S generation suppression experiment. The conditions for H_2S_{high} generation were as follows: maintenance of (1) an appropriate environment for SRB multiplication (anaerobic condition, temperature for mesophilic bacterial growth), (2) high concentration of organic matter, and (3) presence of SO_4.

To maintain condition (1), the column head space was filled with N_2. Valves shown in Figure 1 were shut except for rainwater injection or sampling. Most of the waste layer was filled with rainwater, and the column was set in an incubator (35 °C). To maintain condition (2), organic matter was added to rainwater. To maintain condition (3), SO_4 was introduced into the column in an amount equivalent to approximately 20 times that required for the saturation of $CaSO_4 \cdot 2H_2O$ (approximately 1700 mg-SO_4/L, 17.6 mmol-SO_4/L [22]).

Assuming rainfall at an actual landfill site, artificial rainwater (tap water) was injected with a syringe from the top of the column once every three days. The injected volume was 110 mL every three days, which corresponded to the annual precipitation in Japan, i.e., approximately 1700 mm/y. Organic matter was added to the rainwater (13.6 g-C/L). H_2S in the liquid and gas phases was removed by bubbling N_2 gas when H_2S_{high} was observed. H_2S_{high} observation and H_2S removal were conducted three times as the acclimation stage, and then, the H_2S generation suppression test was performed.

In NR, NO_3 reagent was added to the rainwater (19.05 g-$NaNO_3$/L). In NC, the waste layer was overlaid with approximately 150 g of compost. NO_3 in the compost was leached and transported to the waste layer by rainfall. The compost was replaced once every six days. In OX, two methods of O_2 supply were adopted, i.e., rainwater was aerated to saturate O_2, and air was directly bubbled from the bottom of the column. In air bubbling, air in an empty plastic bottle was introduced into the column by a closed system in order to prevent leakage of H_2S from the column (Figure 2).
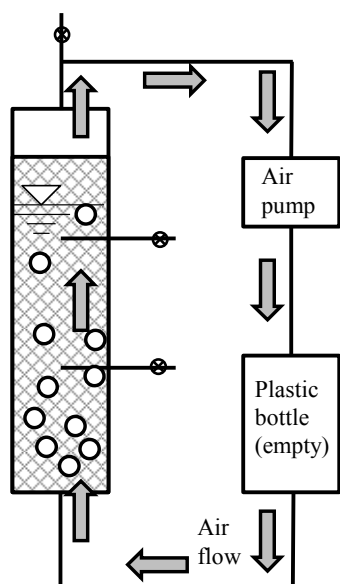

Figure 2. Schematic diagram of air bubbling (OX).

2.5. Analytical Procedure

The objects of measurement were the gas and liquid phases in the column. Measurement items for the gas phase were H_2S concentration and gas volume. Measurement items for the liquid phase were pH, electric conductivity (EC), ORP, dissolved oxygen (DO), TOC, NO_3 concentration, and liquid volume. Sampling was conducted once every three days.

In regard to the gas phase, H_2S was measured with a portable gas detector for worker safety (XS-2200, controlled potential electrolysis, NEW COSMOS ELECTRIC CO., LTD.). Gas volume in the plastic syringe was measured by reading the scale of the syringe.

In regard to the liquid phase, HORIBA B-212 (pH), HORIBA B-173 (EC), HORIBA-D-55 and 9300-10D (ORP), HORIBA-D-55 and 9520-10D (DO), Shimadzu TOC-V_{WS} (TOC), and Thermo Fisher Scientific ICS−1100 (NO_3) were used. Liquid volume was estimated by measuring the gross weight of the column. One hundred and ten milliliters of liquid was sampled from the liquid sampling points (Figure 1) with a plastic syringe. H_2S in the liquid phase was measured by head space sampling.

3. Results

The cumulative amounts of oxygen added (O of NO_3 or O_2) are shown in Figure 3. The unit is mmol-O/L, i.e., added oxygen/liquid volume in the column. The amount in NR was calculated from the amount of $NaNO_3$ added. The amount in NC was determined by calculating the difference between the original amount of compost NO_3 and the residual amount. The amount in OX was determined by calculating the difference of DO in water in the column between before and after aeration. The cumulative amounts of oxygen added exceeded 300 mmol-O/L in NR and NC on day 75, although it was only approximately 2 mmol-O/L in OX.

Changes in H_2S concentration and ORP in control, NR, NC, and OX at the lower point of the column are shown in Figures 4 to 7, respectively (* means N_2 gas bubbling). pH ranged from 5.2 to 8.9, showed an increase with time, and was around 8 after 40 days. EC ranged from 2.7 to 14.8 mS/cm, and was increased with time upon the addition of solution.
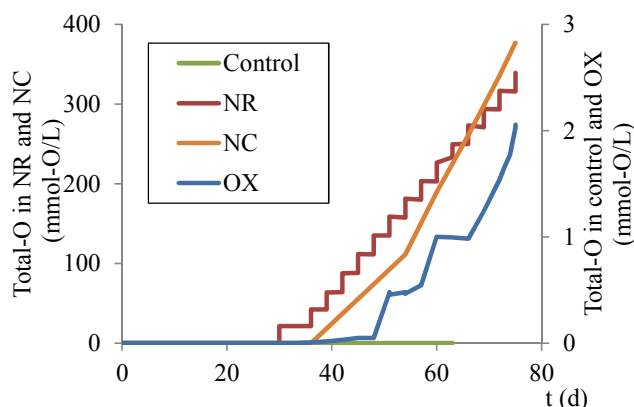

Figure 3. Cumulative amounts of oxygen added.

3.1. Control

ORP in control was below −300 mV (standard hydrogen electrode) after day 10 and H_2S_{high} was generated repeatedly (Figure 4). Thereafter, ORP was increased from approximately −500 to −400 mV, although the reason was unknown. The average ORP after 50 days was −356 mV. H_2S

was rapidly regenerated after removal by bubbling N_2 gas.

3.2. NR: Nitrate (Reagent) Addition

ORP in NR was increased upon the addition of NO_3 (Figure 5). H_2S_{high} was generated and ORP was below −200 mV from day 30 to day 52. After day 52, ORP exceeded −200 mV three times and no H_2S_{high} was generated. The average ORP after 50 days was −283 mV.

3.3. NC: Nitrate (Compost) Addition

ORP in NC was increased repeatedly upon the addition of compost (Figure 6). However, the average ORP after 50 days

was −316 mV, i.e., almost the same as that of control. H_2S_{high} was generated repeatedly.

3.4. OX: Oxygen Addition

ORP in OX was increased drastically upon the addition of oxygen (Figure 7). H_2S_{high} was generated repeatedly from day 36 to day 51 during which O_2 was introduced by adding saturated water. However, the average ORP after 50 days was −166 mV. Thereafter, O_2 was added by air bubbling and H_2S generation was decreased.
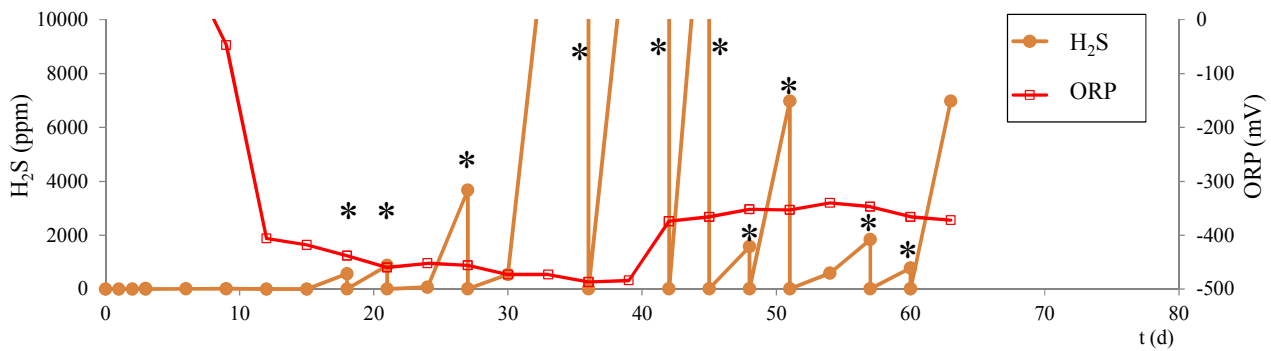

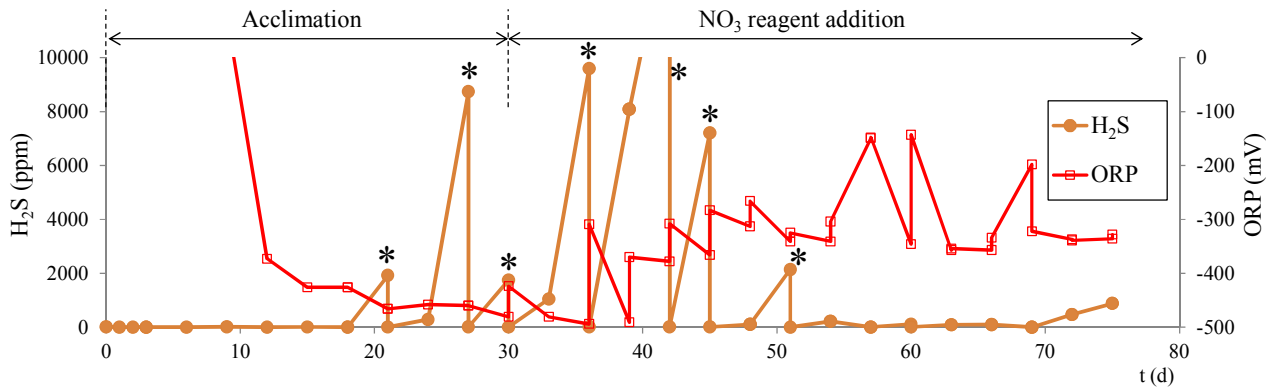**Figure 4.** *ORP and H_2S concentration changes in control.*

Figure 5. *ORP and H_2S concentration changes in control.*
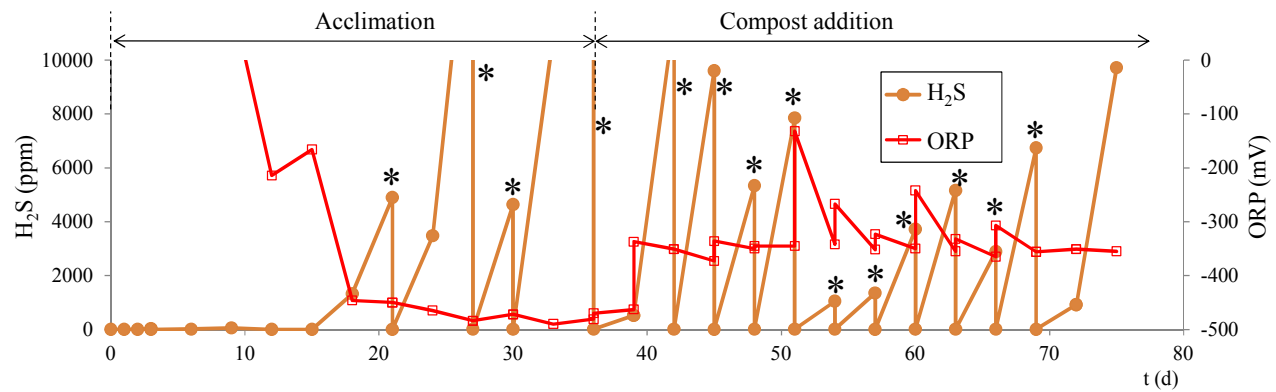

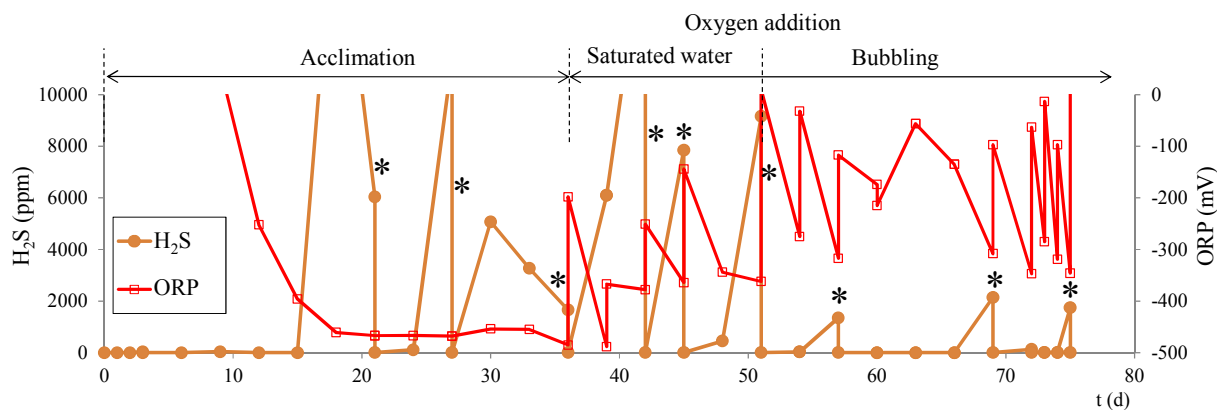**Figure 6.** *ORP and H_2S concentration changes in control.*

Figure 7. ORP and H_2S concentration changes in control.

4. Discussion

4.1. Quantitative Evaluation of H_2S Generation Suppression

The effects of NO_3 or O_2 addition on H_2S generation suppression were quantitatively estimated as follows. The cumulative amounts of H_2S generated are shown in Figure 8. The cumulative amount was determined from the total amount of H_2S in the column and the amount of H_2S removed by bubbling N_2 gas. It is known that H_2S exists in not only the gas phase but also the liquid phase. Therefore, the total amount of H_2S in the column was equivalent to the amounts in the gas and liquid phases. However, only the concentration of H_2S in the gas phase was measured. Using the concentration in the gas phase (determined by taking the average of the concentrations measured at the top, upper, lower, and bottom parts of the column), 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 [23]. As H_2S was generated from the liquid phase, the amount generated (mmol-H_2S) was converted into the amount per unit liquid volume (mmol-H_2S/L). The cumulative amounts on day 60 in control, NR, NC, and OX were 69, 26, 71, and 31 mmol-H_2S/L, respectively. The amounts in NR and OX were half that in control. However, the amount in NC was approximately the same as that in control. The effects of H_2S generation suppression were observed in NR after 45 days and in OX after 50 days. In NR, ORP exceeded −200 mV after 45 days and the suppression effect was observed. In OX, air bubbling was started after 50 days and the suppression effect was also observed. Therefore, the H_2S generation rates from days 50 to 60 were calculated. The generation rates in control, NR, NC, and OX were 0.86, 0.019, 0.75, and 0.041 mmol-H_2S/(L·d), respectively, and the rates in NR, NC, and OX were 0.02, 0.9, and 0.05 times that in control. In this way, the H_2S generation suppression effects of NO_3 reagent addition were observed.

The purpose of this study was to estimate suppression effects not in a complete mixing system, but in column percolation experiments. H_2S concentration distributions in the

height direction (median value from days 50 to 70) are shown in Figure 9. In NR, although NO_3 was injected from the top of the column, H_2S concentrations at the lower and bottom parts of the column were not high compared with the top and upper parts, i.e., the suppression effect reached the deep layer. In NC, although no suppression effect was observed according to the cumulative amounts of H_2S generated mentioned above, H_2S concentrations at the top and upper parts were low (< 20 ppm), i.e., the suppression effect was observed in the shallow layer. In OX, H_2S concentrations at all the sampling points were low (< 20 ppm). The reason was probably because O_2 was supplied to all the column layers by injecting air from the bottom to the top.
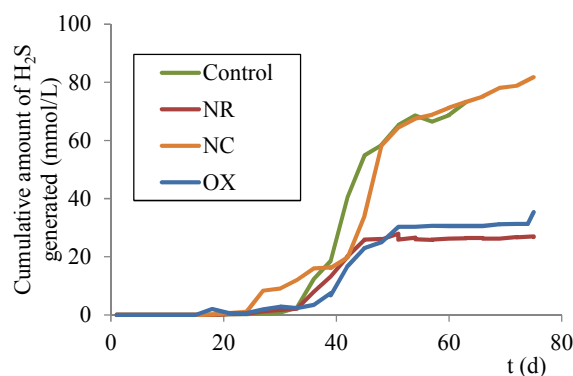

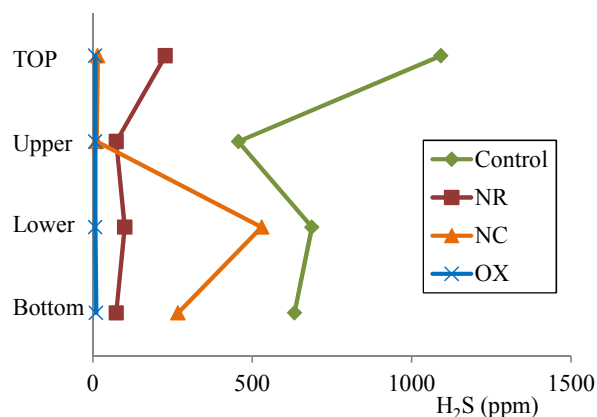Figure 8. Cumulative amounts of H_2S generated.

Figure 9. H_2S concentration distributions (median value from day 50 to day 70).

4.2. Problems Encountered, Application of Results, and Future Issues

In this study, H_2S generation suppression effects were estimated not in a complete mixing system, but in column percolation experiments. In our previous investigation, as we could control NO_3 concentration in the liquid phase in the complete mixing system, the relationship between H_2S generation suppression effect and NO_3 concentration (reagent and compost-derived) could be expressed [21]. In this study, as the concentration of H_2S or NO_3 varied with column depth, concentration control was difficult. Therefore, only the cumulative amounts of oxygen added and H_2S generated could be determined, and the suppression effects of NO_3 or O_2 addition were simply compared. Even though the amount of O_2 added was much smaller than that of NO_3 added, the suppression effect of O_2 was as high as that of NO_3. However, the suppression effect by injecting rainwater saturated with O_2 was low. Assuming a closed system, such as the column percolation experiment used in this study, the whole prepared air could be introduced by bubbling into the system. However, an actual landfill site is an open system. Assuming that air is bubbled into the H_2S generating zone in the waste layer, it would take a long time to dissolve O_2 in water and the air would diffuse out of the zone. Therefore, O_2 injection is difficult. It is difficult to compare the suppression effects of NO_3 and O_2 while taking the ease of injection into consideration.

The amount of NO_3 to be added to a waste layer of a landfill site where H_2S is generated could be estimated from the results of this study. Because the suppression effect of NO_3 injection from the top of the waste layer reached not only the shallow layer but also the deep layer, it is suggested that the NO_3 injection method from the top of the waste layer would be possible also at an actual landfill site. In other words, we could dispense with the NO_3 injection method by introducing pipes deep into the waste layer.

Future issues are as follows. In regard to NC, although the same amount of NO_3 was added as in NR, no suppression effect on the cumulative amount of H_2S generated was observed. Some substances contained in compost would hinder the suppression effect. Considering NO_3 injection into an actual landfill site, the utilization of not NO_3 reagent but useless NO_3 in the market should be considered. Therefore, it is necessary to investigate factors hindering the suppression effect and the possibility of utilizing useless NO_3 in the market, which has sufficient suppression effect. Environmental loading, such as eutrophication by application of the NO_3 addition method at a pilot scale or an actual landfill site, and cost reduction by using useless NO_3 in the market should be evaluated. As NO_3 addition is an alternative method for supplying oxygen, its advantages should be evaluated quantitatively. The advantages include no consumption of large amounts of NO_3 in the aerobic zone and consumption of organic matter by denitrification.

5. Conclusion

In this study, the H_2S generation suppression effects of NO_3 addition using reagent (NR) and compost (NC), and O_2 supply (OX) were quantitatively estimated in column percolation experiments.

The cumulative amounts of oxygen added exceeded 300 mmol-O/L in NR and NC, and approximately 2 mmol-O/L in OX on day 75. The cumulative amounts of H_2S generated on day 60 in control, NR, NC, and OX were 69, 26, 71, and 31 mmol-H_2S/L, respectively. The amounts in NR and OX were half that in control. However, the amount in NC was approximately the same as that in control. H_2S generation rates from day 50 to day 60 in control, NR, NC, and OX were 0.86, 0.019, 0.75, and 0.041 mmol-H_2S/(L·d), respectively, and the rates in NR, NC, and OX were 0.02, 0.9, and 0.05 times that in control. In this way, the H_2S generation suppression effects of NO_3 reagent addition were observed. In NR, although NO_3 was injected from the top of the column, the suppression effect reached the deep layer.

Acknowledgement

References

[1] Lee, S., Xu, Q., Booth, M., Townsend, T.G., Chadik, P., Bitton, G., 2006. Reduced sulfur compounds in gas from construction and demolition debris landfills. Waste Management 26, 526–533.

[2] Eun, S., Reinhart, D.R., Cooper, C.D., Townsend, T.G., Faour, A., 2007. Hydrogen sulfide flux measurements from construction and demolition debris (C&D) landfills. Waste Management 27, 220–227.

[3] Xu, Q., Townsend, T., Reinhart, D., 2010. Attenuation of hydrogen sulfide at construction and demolition debris landfills using alternative cover materials. Waste Management 30(4), 660–666.

[4] Fang, J.J., Yang, N., Cen, D.Y., Shao, L.M., He, P.J., 2012. Odor compounds from different sources of landfill: Characterization and source identification. Waste Management 32, 1401–1410.

[5] López, A., Lobo, A., 2014. Emissions of C&D refuse in landfills: A European case. Waste Management 34, 1446–1454.

[6] Yue, E., Han, B., Sun, Y., Yang, T., 2014. Sulfide emissions from different areas of a municipal solid waste landfill in China. Waste Management 34, 1041–1044.

[7] Milby, T.H., Baselt, R.C., 1999. Hydrogen Sulfide Poisoning: Clarification of Some Controversial Issues. American Journal of Industrial Medicine 35, 192–195.

[8] Townsend, T., Tolaymat, T., Leo, K., Jambeck, J., 2004. Heavy metals in recovered fines from construction and demolition debris recycling facilities in Florida. Science of the Total Environment 332, 1–11.

[9] Townsend, T., Jambeck, J., Jang, Y., Plaza, C., Xu, Q., Clark, C., 2005. C&D Waste Landfill in Florida: Assessment of True Impact and Exploration of Innovative Control Techniques. Florida Center for Solid and Hazardous Waste Management, Gainesville, FL, USA.

[10] Jang, Y.C., Townsend, T., 2001. Sulfate leaching from recovered construction and demolition debris fines. Advances in Environmental Research 5(3), 203–217.

[11] Masamoto, H., Matsukiyo, A., Shigematsu, M., Matsufuji, Y., Yanase, R., 2012. Suppression of Hydrogen Sulfide Release from Waste Plasterboard Disposal in a Landfill-type Lysimeter. Journal of the Japan Society of Waste Management Experts 23(3), 144–153. (in Japanese)

[12] Naruoka, T., Ono, Y., 2004. Control measures against hydrogen sulfide production in final landfill sites. Journal of National Environmental Research 29(4), 14–19. (in Japanese)

[13] Bergersen, O., Haarstad, K., 2014. Treating landfill gas hydrogen sulphide with mineral wool waste (MWW) and rod mill waste (RMW). Waste Management 34, 141–147.

[14] Adib, F., Bagreev, A., Bandosz, T.J., 1999. Effect of Surface Characteristics of Wood-Based Activated Carbons on Adsorption of Hydrogen Sulfide. Journal of Colloid and Interface Science 214(2), 407–415.

[15] Karge, H.G., Raskó, J., 1978. Hydrogen sulfide adsorption on faujasite-type zeolites with systematically varied Si-Al ratios. Journal of Colloid and Interface Science 64(3), 522–532.

[16] Bentzen, G., Smit, A.T., Bennett, D., Webster, N.J., Reinholt, F., Sletholt, E., Hobsont, J., 1995. Controlled dosing of nitrate for prevention of H$_2$S in a sewer network and the effects on the subsequent treatment processes. Water Science and Technology 31(7), 293–302.

[17] Zhang, L., Schryver, P.D., Gusseme, B.D., Muynck, W.D., Boon, N., Verstraete, W., 2008. Chemical and biological technologies for hydrogen sulfide emission control in sewer systems: A review. Water Research 42, 1–12.

[18] Stumm, W., Morgan, J.J., 1996. Aquatic chemistry -Third Edition, John Wiley & Sons, New York.

[19] Farrell, M., Jones, D.L., 2010. Food waste composting: Its use as a peat replacement. Waste Management 30, 1495–1501.

[20] Hasan, K.M.M., Sarkar, G., Alamgir, M., Bari, Q.H., Haedrich, G., 2010. Study on the quality and stability of compost through a Demo Compost Plant. Waste Management 32, 2046–2055.

[21] Kitazaki, S., Xiao, K., Nakagawa, K., Kindaichi, T., Asakura. H., 2014. Hydrogen sulfide generation suppression by nitrate addition – application to solid waste landfill site. American Journal of Environmental Protection 3(5), 267–274.

[22] American Chemical Society, 2006. Reagent chemicals: specifications and procedures: American Chemical Society specifications, Oxford University Press. p. 242.

[23] Ono, Y., Tanaka, N., 2003. Preventing hazardous-level generation of hydrogen sulfide gas in landfill sites: Possibilities and administrative criteria. Journal of the Japan Society of Waste Management Experts 14(5), 248–257. (in Japanese).