



# An Experimental Study on Chemical Oxidative Active Solution for Improving Odorant Deodorization

Hyungduk Lim<sup>1</sup>, Kihun Nam<sup>2\*</sup>, Mailan Arachchige Don Rajitha Kawshalya<sup>3</sup>

<sup>1</sup>*Department of Emergency and Disaster Management, Inje University, 197 Inje-ro, Gimhae-si, Gyungnam, South Korea, neo-crash@naver.com*

<sup>2</sup>*Department of Fire and Disaster Prevention Engineering, Changshin University, Changwon-si, Gyungnam, South Korea, khnam@cs.ac.kr*

<sup>3</sup>*Department of Emergency and Disaster Management, Inje University, 197 Inje-ro, Gimhae-si, Gyungnam, South Korea, rk3omri@gmail.com*

To stop flammable gasses and hazardous materials from igniting and causing mishaps related to leaks, odorants are applied. Gas firms occasionally release gas into the environment while inspecting and maintaining their facilities. The vented gas's odors can lead to a number of issues, such as false complaints of leaks of gas and resident uneasiness. In order to solve this issue, we conducted an oxidation technique experiment to investigate active solutions with the goal of improving odorant deodorization. An oxidation process might be used to successfully eliminate the odor at the site by utilizing sodium hypochlorite, a typical active solution for gas odorants, in conjunction with a deodorizing apparatus fitted with a Venturi-type tube and serial-connection mixed column. The active liquid for oxidizing in this experiment, sodium hypochlorite, can irritate skin and exhibit lingering toxicity. This study found that hypochlorous acid (HOCL), a very safe and environmentally acceptable alternative to sodium hypochlorite, may be used as an active solution to remove smells. As a result, the oxidative technique created here can support efficient management of gas plant safety and shield citizens from complaints.

**Keywords:** Odorant, Active solution, Venturi, Oxidative reaction, Sodium Hypochlorite, Hypochlorous acid.

## 1. INTRODUCTION

Organic sulfur compounds, or odorants, are frequently found in city natural gas and liquefied petroleum gas (LPG) and serve as warning systems in the event of a gas leak (Kim et al., 2014; Kim et al., 2014; Natural Gas Odorizing, 1997). According to Tomoko et al. (2016), an odorant is an additive used with hazardous materials and flammable gasses to stop leaks and associated safety incidents. The addition of an odorant serves as a warning mechanism for gas. When safety precautions are taken, odorants help identify leaks and encourage the

safe use of gases by averting mishaps. In Table 1, odorants' attributes are displayed. Depending on the gas company, different odorants are applied. The firm also sets and maintains the standard quantity injected. THT [ $C_4H_8S$ ] and TBM [ $(CH_3)_3CSH$ ] are the odorants that are employed in Korea. When doing facility maintenance and inspections, gas firms occasionally release gas into the environment (Zanchettin et al. 2014). However, the public believes that the smell of the vented gases indicates a gas leak, therefore they often notify the local authorities right once. The public's apprehension over odorants poses significant challenges for operators of gas facilities.

Table 1: The characteristics of smell for odorant

Product name	Molecular formula	Odor characters
Tetrahydrothiophene (THT)	$C_4H_8S$	gassy
Tertio Butyl Mercaptan (TBM)	$(CH_3)_3CSH$	gassy
Dimethyl sulfide (DMS)	$CH_3SCH_3$	unpleasant/gassy
Ethyl Mercaptan (EM)	$C_2H_5SH$	gassy
Methyl Ethyl Sulfide (MES)	$CH_3SC_2H_5$	unpleasant/gassy

By assessing the technological viability of employing active solutions, we investigated strategies for enhancing the the deodorization for odorants in gases in order to solve the problems related to odorants. Among the chemical deodorization techniques used in this study are the use of sodium sulfite, an oxidant solution cleaning technique, and an acid/alkali washing approach employing chlorine oxide. The most significant development in deodorization technology has been the ability to combine oxidation methods, including those utilizing ozone as well as chlorine dioxide, with the cleaning approach based on reducing agent solutions in a variety of ways. To enhance the the deodorization for odorants in gasses, we explored the oxidation approach as a means of breaking down and eliminating offensive materials that prove challenging to eliminate using water. The major ingredients utilized for adding a neutralizer to a substance that oxidizes are hypochlorite of sodium, chlorine, and ozone. Ammonia, hydrogen sulfide, a substance called and amines are the primary target gases for the oxidation technique among odorous chemicals (Lee & Roh, 2019; Won & Shin, 2019).

The oxidizing chemical itself smells bad, which is the primary issue with the oxidation process. The odor component determines which solution is best, and the odor component's solubility as well as reaction rate are important factors to take into account. Furthermore, a non-toxic solution is preferred, and it cannot be poisonous. Maintenance may be challenging if waste liquid emitted after deodorization needs to be post-treated (Lee & Roh, 2019; Wysocka et al., 2019).

## 2. METHODOLOGY

In this investigation, oxidation was employed to eliminate the natural gas smell using sodium hypochlorite. By consulting the desorption and adsorption diagrams of earlier research, a basic deodorizing and dispersion device was created, with the odorant concentration being determined by references (Jung et al, 2009).

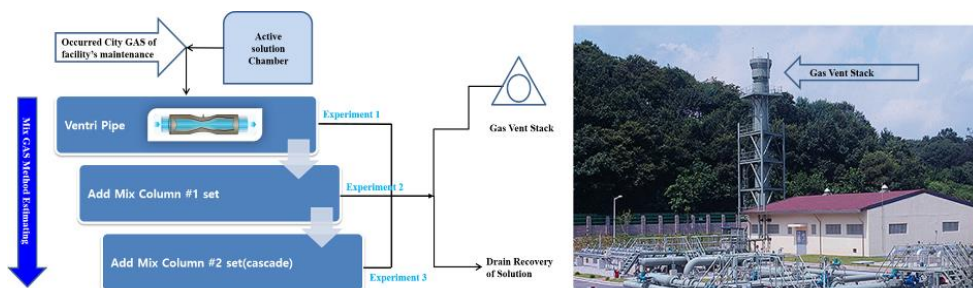


Fig. 1: Research methodology

The deodorizing technique we use lowers the pressure (0.8–1.0 MPa) over a sodium hypochlorite solution by using gas flow. Where R is a hydrocarbons structure and SH is a mercaptan, the hypochlorite and odorant react as  $R-SH + 4Na_2ClO \rightarrow Na_2SO_4 + 4NaCl$  (Sharif et al., 2012). After H is eliminated, the oxidizer and odorant pass through a nozzle in the mixture's column and undergo oxidative breakdown to C. After that, the discharge pipe is used to release the deodorized natural gas into the sky. In accordance with Fig. 1, the system was put into practice after being empirically optimized.

### 3. RESULT

Gas is discharged at a rate of 50 Nm<sup>3</sup> via a pipeline valve onto a discharge hose during repairs when the supply of gas facility maintenance requires the venting of gas from the pipeline (usually done 30 times a year) and a gas recovery system hasn't been used. Installing a gas recovering system reduces gas leaking by around half and maintains the other valve at roughly 20 Nm<sup>3</sup>. Natural gas releases for general maintenance are normally stopped within ten minutes after replacing nitrogen gas to provide safe operating conditions. Within the range of 0.8 and 1.0 MPa, the dissipated gas pressure exists. A basic dispersion and deodorizing apparatus was created and experimentally refined to effectively blend the oxidizing agent and natural gas odorant. To guard against corrosion caused by sodium hypochlorite, the apparatus was constructed using stainless steel alloy 304SUS.

#### 3.1 Device composed of simple pipe and a single mixer (Experiment 1)

A nozzle fixed to a regular cylindrical pipe allowed oxidant to be introduced into the mixture's column along with municipal gas. The gas normally evacuated within 10 minutes without reacting with the oxidant because of the high feed rate. As can be seen in Fig. 2, the odorant concentration was around 2/8 ppm, which is the normal amount given to the municipal gas supply. The findings of this procedure, which were repeated twice, showed that considerable improvements were required.

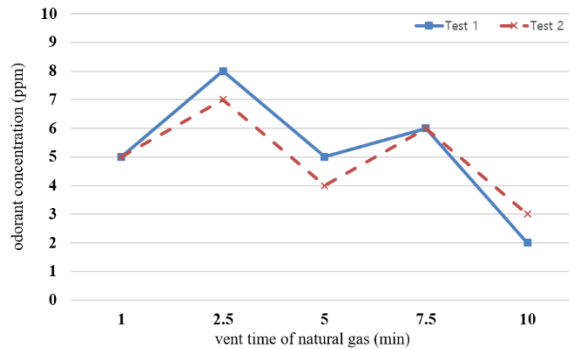


Fig. 2: Odorant concentration (experiment 1)

### 3.2 Device composed of a Venturi tube and Single Mixer (Experiment 2)

The conventional pipe was swapped out for a Venturi tube in Experiment 1 to address the insufficient mixing issue. The gas flow (0.8–1.0 MPa) was utilized to reduce the pressure within the sodium hypochlorite solution. As a result, as the input gas moved through the mix column, hypochlorite could be combined with it. Condensed and remixed surplus mixed gas might then be released into the environment. A tube that progressively reduces and then expands in diameter is known as a venturi tube. Fluid is drawn into the narrow section due to the pressure differential that exists between wide and small sections. We refer to this phenomenon as the Venturi effect.

Air traveling through the Venturi tube narrows and gains velocity while losing pressure at the same time. A sufficient mixing with the city gas is made possible by the low pressure that causes the oxidant solution to be sucked into a Venturi tube and atomized. Hyang-lax, a hypochlorite solution with 12% aqueous chlorine, produced a rather overpowering chlorine fragrance even though the odorant was effectively eliminated by this technique. The Hyang-lax 2:1 was diluted by using water in four different studies to lessen this. Regrettably, there was still too much chlorine in the liquid being expelled from the mixer even after dilution. The test findings displayed in Fig. 3 suggest that after going through the deodorizing equipment, there was a slight reduction in odorant (concentration of  $> 1$  ppm). But in one instance, during gas venting, the active solution mixed too much, causing the combination to be expelled. A concentration of around 1 ppm of odor was used in four studies.

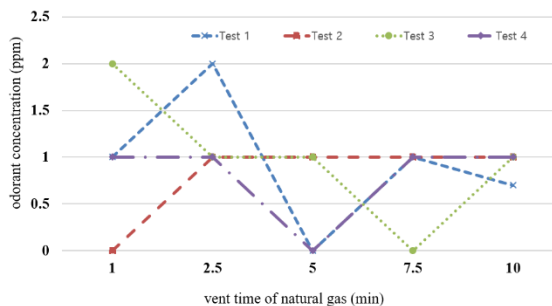


Fig. 3: Odorant concentration (experiment 2)

3.3 Device composed of a Venturi tube and two mixers (Experiment 3)

The secondary mixer was utilized to more successfully differentiate the deodorized gas that was departing the top part of the mixers from the solution of hypochlorite that was being released from the bottom with the mixer, therefore resolving the issue of overmixing that had been seen in Experiment 2.

Furthermore, by connecting the Venturi tube to the city gas pressure, a smooth injection into the oxidant the solution was guaranteed. The amount of mixing may be changed in this manner by using the control valve located in the center of the tube. As seen in Fig. 4, the odorant was completely eliminated (0 ppm) from city gas as a consequence of using this system. To establish validity, this experiment was conducted four times.

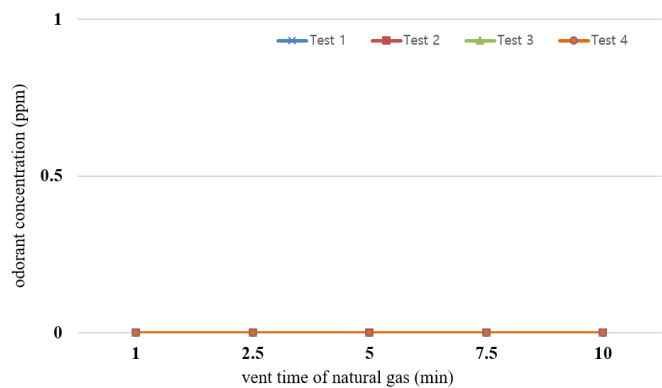


Fig. 4: Odorant concentration (experiment 3)

The finished deodorizing apparatus is depicted in Fig. 5 based on the aforementioned experimental findings. A Venturi tube was used to introduce an oxidizing solution including sodium hypochlorite into the city gas. ②After going through the injection tube, the tube enables for improved deodorant dispersion by altering the city gas's flow velocity. ④ into the primary mixer ③. As the oxidant solution ① is combined with the municipal gas; any remaining mixture is gathered at the mixer's bottom and routed via tubes. ⑤ and ⑧. The addition of a porous plate ⑦ in the secondary mixer ⑥ enhanced the effectiveness of mixing. Ports are used to release deodorized municipal gas. ⑨Figure 6 depicts the deodorizing device in use for actual gas plant repairs.

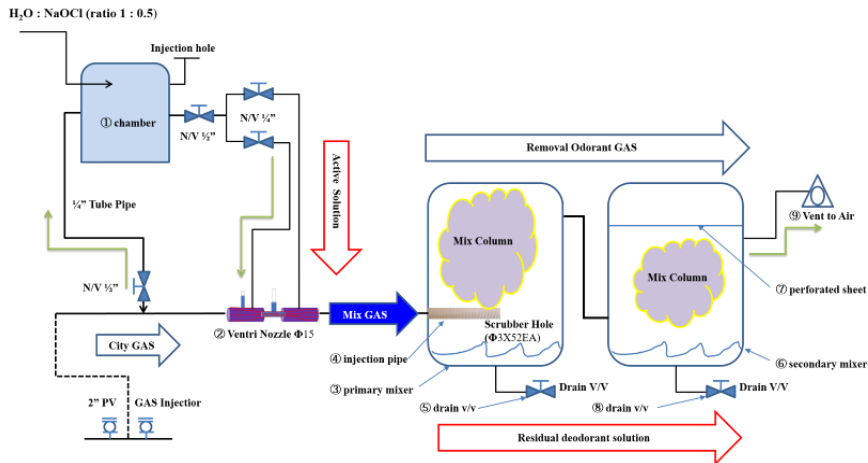


Fig. 5: Process for simple ventilation device of odorant removal



Fig. 6: Compact gas scrubbing equipment

## 4. Discussion

Gas providers frequently have to pipe gas into the atmosphere or perform emergency repairs and inspections that require venting gas within buildings. Gas is odorless and colorless, therefore in order to detect leaks, it is frequently legally required to combine it in a certain ratio with an odorant. The public interprets the smell of gas being released during maintenance as being suggestive about a gas leak; it can cause issues because of fabricated claims of leaks and resident apprehension. In this study, an active solution was used to deodorize odorants in order to solve this issue.

### 4.1 Removal of odor in natural gas using sodium hypochlorite as the active solution

The active solution used to address the stench of municipal gas, sodium hypochlorite (NaOCl), is administered on site together with a basic deodorizing and discharging equipment to successfully eliminate the odor in natural gas. A venturi tube and the cascade mixing method are also used in the deodorization process. The venturi effect was used to increase mixing by creating negative pressure in the Venturi tube as a result of the gas velocity (0.8–1.0 MPa) with the presence of sodium hypochlorite inside the solution container. Using a porous nozzle, the gas and solution were combined again in the mix column, and the liquid that was produced by the leftover solution was drained out of the column.

Using the hose, the gas that had been totally cleared of the stink was released into the surrounding air. A mixture of is (i-C<sub>4</sub>H<sub>10</sub>) detector for gases (COSMOS XP-3160) used to measure the odorous substance frequency in the hose resulted in a value of 0 ppm, indicating that the odorant had been eliminated. Employing a precise gas detector (COSMOS XP-3160) calibrated to isobutane (i-C<sub>4</sub>H<sub>10</sub>), the odorant concentration in the discharge hose was determined, as previously mentioned.  $R-SH + 4Na_2ClO \rightarrow Na_2SO_4 + 4NaCl$  is the deodorizing process that produced trace quantities of sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>) as well as sodium chloride (NaCl), where R and SH stand for hydrocarbons and mercaptan systems, respectively. Prior to discharge as well as disposal, the deodorization solutions was diluted with water. In place of more traditional techniques for removing gas odor, such as adsorption of activated carbon or combustion utilizing a flare stack, this study presented an oxidation approach utilizing an active solution containing sodium hypochlorite. Large volumes of high-pressured gas must be released in the event of a gas plant emergency and when building plans call for connecting a long-distance pipe between shut-off valves. In these cases, combining the active solution with a basic container or pipe (passage) is insufficient. For spraying the active ingredient solution as tiny particles, as needed for this investigation, other parts are also needed, including a Venturi pipe.

#### 4.2 Safety of Active Substances and Possible Alternative Substances

During this investigation, sodium hypochlorite (NaOCl), a hypochlorite salt produced by absorption chlorine dioxide into a sodium hydroxide solution, was utilized as an active solution. This aqueous solution, which has an appearance ranging from light yellow to translucent, is commercially available and contains 4–12% effective chlorine. It is an extremely alkaline liquid that breaks down quickly to liberate oxygen. Because of its ability to oxidize, sodium hypochlorite is employed as an oxidizing, bleaching, and disinfecting agent. Although it costs more than chlorine to disinfect, it is used more frequently than liquid chlorine since it is leak-proof and safe to handle. In addition to causing ocular, respiratory, and skin disorders due to its toxicity, sodium hypochlorite can also be used with diluent and stabilizers (Baur & Bittner, 2009). Similar characteristics apply to the very acidic hypochlorite acid, which has a pH of up to 2.7 and a successful chlorine concentration ranging from 20–60 ppm. Electrolysis is the process that uses just salt and water to create HOCl. It is an ecologically friendly product with a safe disposal method that doesn't harm animals. The most potent of them is hypochlorite acid, which has a sterilizing potency 80 times greater than that of hypochlorite. Hypochlorite acid has sterilizing (or oxidizing) power equal to 1,000 ppm of sodium hypochlorite solution at a successful chlorine level of 40 ppm (Hotta K 1999). Because the odor-removing active solution is combined with gas and



released in large amounts into the soil or environment, safety needs to be taken into account. Hypochlorite acid is favored as a safe and environmentally friendly product due to the caustic and poisonous properties of hypochlorite of sodium and other high-concentration diluents. If considerable amounts of odorants need to be removed, hypochlorite acid is suggested as a substitute active solution for sodium hypochlorite.

## 5. Conclusion

This study aimed to enhance the odorant deodorization process in gases by employing an active solution oxidation approach. Our oxidation approach for gaseous odorants was based on a chemical reaction using sodium hypochlorite, a typical active solution. We had a Venturi tube as well as a serial-connection mixed container attached to our deodorizing apparatus. In the field, odor elimination was verified. Sodium hypochlorite, which was the experiment's active solution for oxidation, has persistent toxicity and can irritate skin. Because it is incredibly safe and environmentally friendly, hypochlorite acid is advised as an active solution replacement to solve this issue. This study offers a technique that could improve gas facilities' stability and safety, reducing resident anxiety and false claims of gas leakage.

## Acknowledgments

This study was supported by the National Research Foundation of Korea (NRF) grant funded by the Korean government (MIST) (No. 2022R1F1A1074289)

## References

1. Baur, X. & Bittner, C., (2009). Occupational obstructive airway diseases caused by the natural gas odorant tetrahydrothiophene—two case reports. *American Journal of Industrial Medicine*. 52(12), 982-986 <https://doi.org/10.1002/ajim.20761>
2. Hotta, K. and Suzuki, T. (1999). Electrolyzed water: Formation principal, physicochemical property and function. *Biosci. Ind.*, 57, 22-26.
3. Jung, G. S., Lee, S. H., Cheon, J. K. Choe, J. W. & Woo, H. C. (2009). Adsorptive Removal of TBM and THT Using Ion-exchanged NaY Zeolites -Clean Technology. *CLEAN TECHNOLOGY*, 15(1), 60–66.
4. Kim, J. K., Yim, E. S., Min, K. I. & Jung, C. S. (2014). A study on the Performance and Exhaust Emissions Characteristics of LPG Engine using LPG Fuel with New Sulfur Free Odorant. *Journal of Energy Engineering*, 23(3), 88–95. <https://doi.org/10.5855/ENERGY.2014.23.3.088>
5. Kim, J. K., Yim, E. S. & Jung, C. S. (2014). A Study on the Application of Sulfur-Free Odorant for LPG Fuel. *Journal of the Korean Institute of Gas*, 18(5), 52–59. <https://doi.org/10.7842/kgas.2014.18.5.52>
6. Lee, S. L. & Roh, N. J. (2019). A Study on Strengthening the Competitiveness of Korea's Natural Gas Industry in Response to Structural Changes in Global Natural Gas Markets (3/3). Korea Energy Economics Institute.
7. *Natural Gas Odorizing, Inc. v. Downs :: 1997 :: Indiana Court of Appeals Decisions :: Indiana Case Law :: Indiana Law :: US Law :: Justia.* (n.d.). Retrieved June 19, 2022, from <https://law.justia.com/cases/indiana/court-of-appeals/1997/61a01-9612-cv-396-8.html>
8. Sharif, A. A. M., Astaraki, A. M., Azar, P. A., Khorrami, S. A. & Moradi, S. (2012). The effect of NaCl and Na<sub>2</sub>SO<sub>4</sub> concentration in aqueous phase on the phase inversion temperature O/W nanoemulsions. *Arabian Journal of Chemistry*, 5(1), 41–44.



<https://doi.org/10.1016/J.ARABJC.2010.07.021>

9. Tomoko, M. , Naomi G., Yasushiro G. & Tatsu K., (2016). A method for psychophysical screening of odorants for use in city gas based on olfactory adaptation tolerance. *Chemosensory perception*. 9, 120-130 <https://doi.org/10.1007/s12078-016-9213-3>
10. Won, S. Y., & Shin, H. Y. (2019). A Study on the Odorization Levels and Management in the Facility using Liquified Natural Gas(LNG). *Journal of the Korean Institute of Gas*, 23(6), 25–32. <https://doi.org/10.7842/KIGAS.2019.23.6.25>.
11. Wysocka, I., Gębicki, J. & Namieśnik, J. (2019). Technologies for deodorization of malodorous gases. *Environmental Science and Pollution Research*. 26, 9409–9434. <https://doi.org/10.1007/s11356-019-04195-1>.
12. Zanchettin C., Almeida L. M., & Menezes F. D., (2014). An Intelligent Monitoring System for Natural Gas Odorization. *IEEE Sensors Journal*, 12(1), 425-433 <http://doi.org/10.1109/JSEN.2014.2345476>