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# Elimination of Odorous Pollutants by the Granulated Soli "Volcanite" Method

By

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## Introduction

Recently, complaints about stinking gases have increased. These gases are produced by materials which have no legal restriction and also come from diverse sources of gas emission. Taking measures against small-scale sources of gas emission and regulating odorous gases based on a sensory evaluation have now proved to be important and necessary[1].

Regarding measures against odorous gases, more technological development is necessary in the following areas: efficiency and economical aspect of the measures against composited odor; expenses of chemicals and electricity; and corrosion and blockage of the deodorizing apparatus. For the measures against small-scale gas emissions, in particular, technological development is necessary to construct a small apparatus which works efficiently, is adjustable to changes in volume and quality of the odorous gas, and has a remover with durable substitutes for a large and structurally complex apparatus[2].

Biological deodorization is a relatively new method which has drawn attention. This method is based on the biochemical mechanism of elimination through microorganisms (mainly bacteria), whereas the current method of elimination of odorous gases is based on the physicochemical processes (i.e. absorption, acidification, and deoxidization). The biological method which is becoming useful for eliminating odorous gases emitted from such sources as sewage and night soil treatment plants, farms, and rendering plants, works on the degeneration of odorants through the combination of assimilation and catabolism. However, many fundamental problems such as the mechanism for

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the behavior and decomposition of odorants in the microorganisms and some operative aspects of the equipment are still unsolved. Moreover, the design of elimination apparatus, which are employed for the actual composited odor, is yet to be standardized[3].

In this paper, we examine a deodorization method utilizing volcanite[5)6] in order to overcome the following problems: since the existing soil deodorization method depends on an extremely small ventilation rate in the soil layer, it requires a large area of filter layer. Besides, blockage of the filter layer may occur due to consolidation settlement, rainfall or decomposed products, which, therefore, necessitate frequent reshuffle or exchange of the soil layer. This paper presents the results of our study which has successfully tackled these problems.

## 1.   The Method of Biological Deodorization and Elimination Mechanism

A deodorization apparatus with a mode of stationary filteration[7] is filled with supporting materials of microorganisms which include the following: soil including Ando-soil and Masa-soil; organic materials such as peat and humid substances; inorganic materials such as ceramic, slag, blast furnace sludge; high molecular compounds such as sponge rubber and plastic net, and granular charcoal. This deodorization apparatus works efficiently to eliminate odorous gases from sewage and night soil treatment plants. These odorants consist of hydrogen sulfide and ammonia with several ppm concentration and are easily deodorized utilizing a biological method. The design of the apparatus, to a large extent, is based on the nitrification rate (5 mg/100 g of soil) against ammonia or the flow rate (5 mm/sec) in the filter layer which are known from experience. The same design of the apparatus is also used by many sewage treatment plants in Japan[8].

The methanism for the conversion of odorants inside the soil layer can be generally explained as the following steps, although the exact process for the conversion of most of the odorous gases except for ammonia[10] has not been examined yet[11]:

1) Absorption of odorants in adhering water or capillary water in the soil layer, and absorption and capture of odorants in the solvent and on the soil surface.

2) Transfer of the odorants captured inside the soil layer into the microorganisms, and biological decomposition inside the microorganisms.

3) Discharge of decomposed materials out of the microorganisms which have been changed or produced by metabolism inside the microorganisms, or accumulation of decomposed materials inside the microorganisms.

4) Washout of decomposed material by sprinkling water.

In this mechanism, the most important rate limiting factor of soil deodorization is the absorption into the soil layer which requires sufficient time. Since the absorption into the holded water in the layer follows the Henry's law, the deodorization effect depends on the dissolution rate of odorants[12]. However, sprinkling water should be introduced intermittently because it tends to block the soil layer[9]. As regards the activated sludge aeration, biological decomposition has been considered as a rate limiting factor[3][13]. However, regarding the decomposition rate and quantity, most hypotheses which relate the mechanism of odorant movement to the mechanism of biological decomposition are subject to further studies and experimental examination.

In a previous paper[14], we studied the elimination effect on odorants and the experimental aspects of volcanite when it is mixed with andosoil and carbonized chaff. Fig. 1 shows the typical behavior of odorants in a layer filled up with volcanite. The elimination mechanism of odorous gases in our method is as follows:
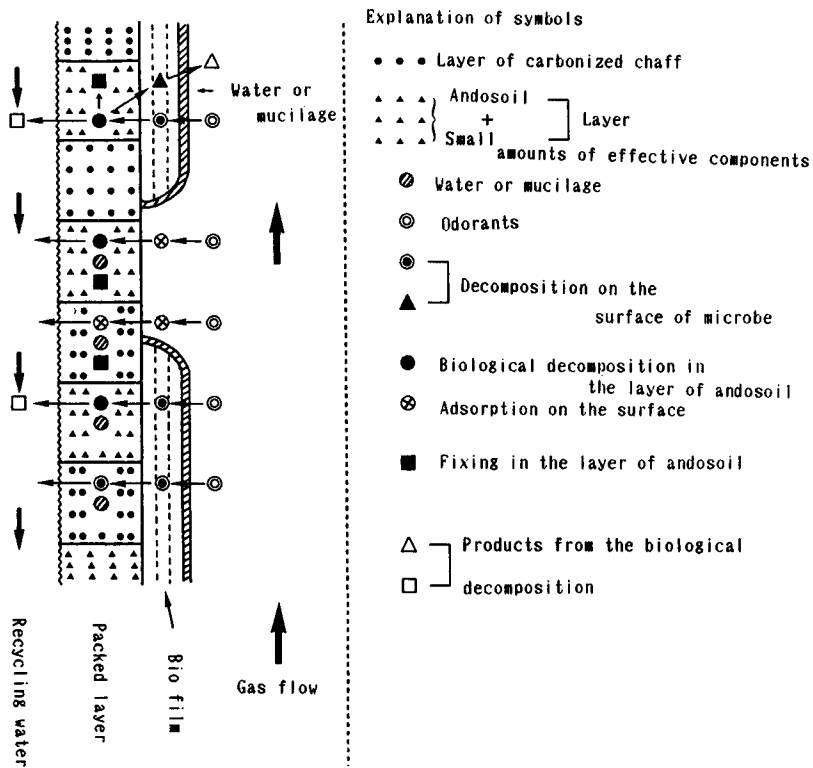


Fig. 1  A typical figure for the mechanism of deodorization by volcanite.

1)   The processes of dissolution and absorption of gaseous odorants in the surface water layer or the mucilage of the microorganisms.

2)   The formation process of secondary products, i.e. odorants dissolved and absorbed in the surface layer of microorganisms are decomposed and converted into other substances through anabolism and catabolism of microorganisms.

3)   Decomposed products and materials moving in the liquid of the surface layer react with the soil elements, or they are attached to the soil particles through absorption.

4)   Decomposed products move in the sprinkling water (i.e. elution), and the elements stabilized (combined) inside the soil layer are eluted, as well.

5)   The odorants with hydrophobic property are absorbed on the surface of soil particles, or they are fixed through combination with the soil elements.

6)   Microorganisms react to decompose the materials fixed in the soil layer, or the odorants with hydrophobic property are converted into secondary products through reaction with the products of biological decomposition.

7)   The fixed components in the soil layer or the products of biological decomposition move in the sprinkling water.

8)   The products of biological decomposition are emitted into the air from the soil layer or from the microorganisms.

The parts of the elimination mechanism of odorous gases described above are supposed to proceed side by side.  Those species of microorganisms which are involved in the biological reaction are large in number and the process is a chain reaction.  And it is supposed that the biomembrane and the biota inside the soil layer are adapted to the quality and quantity of the odorants supplied, the biota increase in number as the species compete with each other or antagonize, and that they turn the odorant into a low molecular compound or change its quality through the chain of the decomposition process.

This indicates that the elimination of a wide range of odorants is possible if the biota are sufficiently acclimatized and arrangements are made for an increase in the temperature, moisture, the nutrient source, oxygen, and buffer action.   Then it is possible for microorganisms to decompose substances such as aromatic hydrocarbon and high molecular aldehyde[5)6)].

It should be noted that the dissolution and absorption to the surface of a biomembrane is not always a rate limiting factor because hydrogen sulfide (with a concentration of about 100 ppm) is completely eliminated when the circulating sprinkling water in the soil layer shows strong acidity (pH of $<1.5$)[17)18)].   It should rather be considered that the mechanism through which microorganisms capture odorants in the surface water is different from the ordinary mechanism

of gas absorption.

Furthermore, the method of soil deodorization is applied to the source of odorants with a relatively lower density, and the efficiency of deodorization extremely decreases as the soil is solidified when hydrogen sulfide is of high density.  It is also necessary to make sufficient contact time by decreasing the wind velocity when a high density of hydrogen sulfide is in treatment, as the rate limitation is caused by absorption to the soil[9].

The velocity of odorous gases moving in the surface water of microorganisms is largely affected by the density of odorants in the air and the chemical properties of the surface water.  However, the movement of odorants is always from a gaseous to a liquid state because the rate of metabolism is very fast at the interface of the liquid side[17][18].     For this reason, it is possible to take odorants completely to the liquid side by increasing the contact surface rather than increasing the contact time in the case when odorants of high density are introduced.   Moreover, we cannot make a judgement on the mechanism for the behavior of substances simply following after the Henry's law which considers fluids as static.  It is believed that even those odorants whose dissolution rates of hydrophobic property are extremely slow would be possibly eliminated.   In other words, further studies are necessary to investigate the movement of odorants from the surface liquid phase of the microorganisms to the inside liquid phase of the microorganisms, and the alteration and movement velocity of odorants.

We are also proceeding with a study on the modeling of an elimination mechanism experimentally based on the behavior of odorants inside the soil layer, both in single and multiple components[19].   In other words, the odor components flowing into the packed bed per unit of volume and time in the biological decomposition apparatus with a packed tower type (i.e. cross section area times minuteness height) are accumulated in a gaseous state or on the surface of base material and are the dissolved; the rest of the odor components flow out of the volume of the packed bed as shown in Fig. 2.

The material balance inside the deodorization tower is formulated as follows:

$$-u\frac{\partial C}{\partial Z} + \varepsilon Ez\frac{\partial^2 C}{\partial Z^2} = r\left\{\frac{\partial Q}{\partial t} + R\right\} + \varepsilon\frac{\partial C}{\partial t} \qquad \cdots(1)$$

where

$C(z,t)$ is the concentration of odor components in ($g$-odor/cm$^3$);
$Q(z,t)$ is the absorption amount of Packing material in ($g$-odor/$g$-Packing material);
$R(z,t)$ is the dissolution velocity in ($g$-odor/$g$-Packing material/sec);
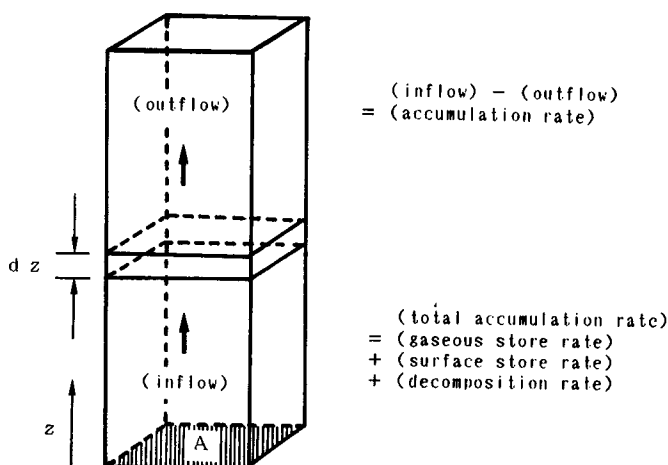
Fig. 2   Mass balance of gaseous odor components in the biological deodorization plant

$z$ is the length of flow direction measured from that side of the bed where odorous components to enter (cm);

$t$ is the passage of time (sec);

$u$ is the velocity of apparent line (cm/sec);

$\varepsilon$ is the void ratio;

$r$ is the packing density ($g$-Packing material/cm$^3$); and

$Ez$ is the mixed diffusion coefficient in flow direction.

Furthermore, the sorption velocity $\left(\dfrac{\delta g}{\delta t}\right)$ is generally given by the following equation in case there is no dissolution reaction of odor components absorbed on the surface of Packing material:

$$r\,\frac{\partial q}{dt} = k_f a_v (Qe - Q) \qquad \cdots (2)$$

where $K_f a_v$ is the overall capacity coefficient, and $Qe$ is the sorption amount at an equilibrium state with the concentration($C$) of gaseous state ($g$-odor/$g$-Packing material).

We are currently carrying out a study on the factors which influence the dynamic sorption of odorants based on the basic equations given above[19].

## 2. Volcanite

Various forms of organisms, inorganic substances, and plastics have so far

been utilized as supporting materials for biological deodorization. These materials are selected keeping in mind the following points: increase in the adhesion area of organisms; decrease in ventilation resistance of odorous gas; capacity of retaining void water (capillary); and physical absorption by hydrophobic materials. Proper strength of apparatus and ventilation are also important criteria because of consolidation, blockage, and back washing of the filter layer and the packed bed[20)21)].

Compared to other methods, the method of soil deodorization which employs Ando-soil, Masa-soil, and loam soil layers and composting materials, requires a larger filter area due to some factors mentioned above; and this has been a major practical drawback for the soil deodorization method since the ventilation resistance of the filter layer is very large. A ventilaltion rate of 5 mm/sec, a thickness of 400–600 mm, and a contact time of 100 sec are standard features of this method[12)]. As there is a limitation on the elimination of odor components in dissolution and absorption of adhesion water or capillary water, the ventilation rate of 10–20 mm/sec is the limitation of the soil deodorization method[9)]. Therefore, a mixture of zeolite, activated charcoal, and slag are examined in order to decrease the ventilation resistance and increase the capacity of capturing odorants[2)].

Volcanite for this experiment was made mainly from Ando-soil in order to produce a buffer effect against dissolution products, to supply nutrients to increased microorganisms, to decrease the ventilation resistance, and to increase the relative surface area. We are proceeding with the further development of this odor elimination plant using volcanite.

The composition of Ando-soil, which was the main material in this experiment, is shown in Table 1. It contains a lot of silisic acid, alumina, iron oxide, and organic matter. Carbonized chaff (with a specific gravity of 0.7 and a relative surface area of 1.24 $m^2/g$), mineral powder and bond were mixed and granulated to make volcanite. Fig. 3 shows the relationship between the average particle size of volcanite and the average particle number per unit volume (IL) which are obtained from multiplying relative surface area measured for each division of particle size (by GC method) by the average number of particles of each division. It is about $7.2 \times 10^3$ $m^2/L$ for the range of particle size 0.2~1 cm. In addition, the surface area of volcanite particles is calculated and plotted in Fig. 4 against the average particle sizes obtained from the average number of particles and the value of relative surface are in Fig. 3. The surface area of volcanite particle is more than $10^4$ times compared to the curves which show the particle as a ball in Fig. 4, and it is found that surface are per unit volume (IL) is $1.4 \times 10^4$ times larger when the particle acts as a ball.

Table 1    Chemical components of andosoil

|                  | Content (wt %)    |
| ---------------- | ----------------- |
| $SiO_2$          | $33.3 \sim 49.4$  |
| $Al_2O_3$        | $16.7 \sim 19.2$  |
| $Fe_2O_3$        | $3.6 \sim 8.9$    |
| $TiO_2$          | $0.3 \sim 1.2$    |
| Zn               | $0.005 \sim 0.007$ |
| Cu               | N.D.              |
| Ca               | $0.2 \sim 2.2$    |
| Mg               | $0.6 \sim 1.0$    |
| Na               | $0.2 \sim 2.1$    |
| K                | $0.6 \sim 1.1$    |
| As               | N.D.              |
| Hg               | N.D.              |
| Organics         | $23.0 \sim 33.9$  |

Note[16];    Specific gavity: $2.08 \sim 2.12$, Surface area:
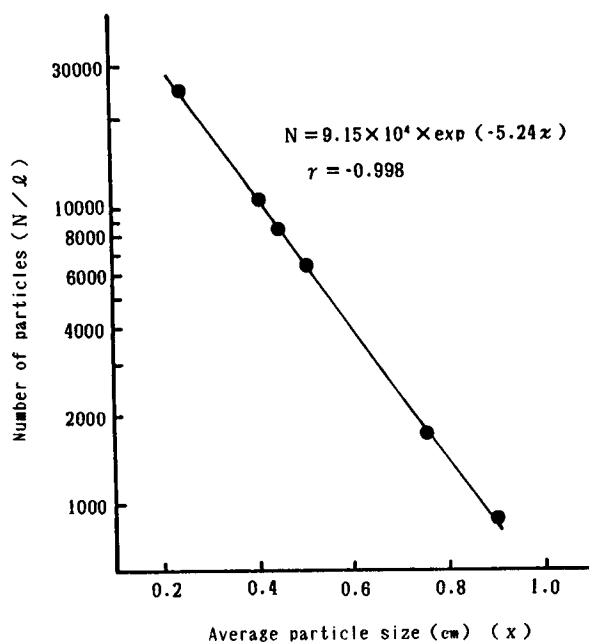$0.46 \ m^2/g$



Fig. 3   The relationships between average particle size and the number of particles per unit volume.
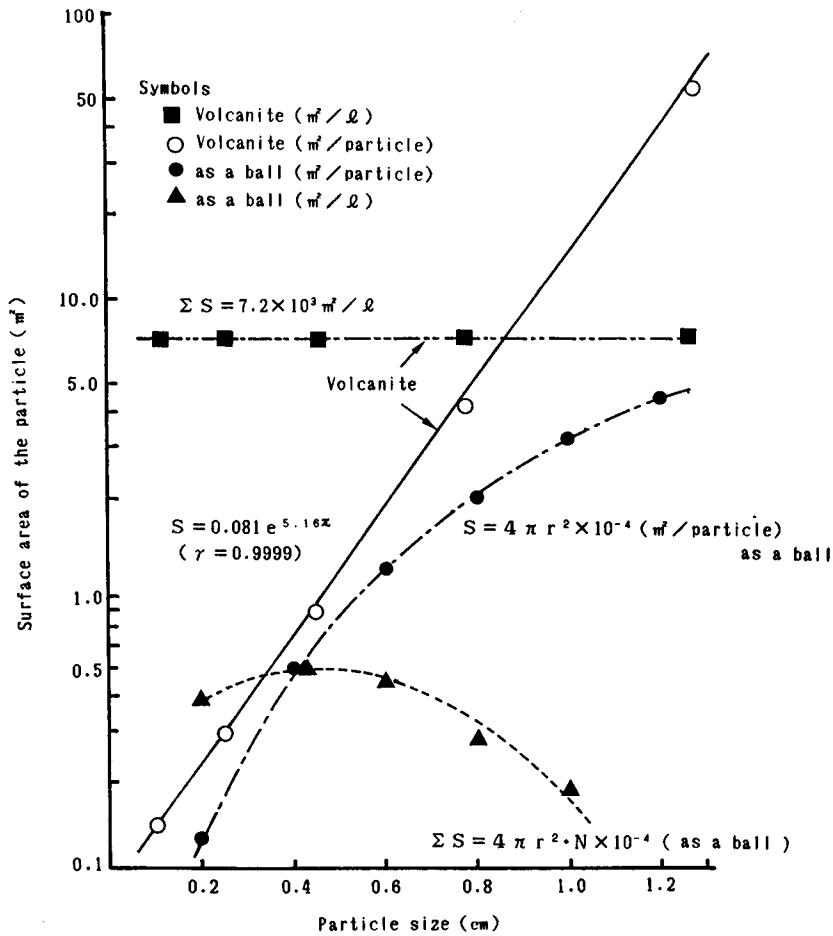
Fig. 4 The surface area of a volcanite particle.

Table 2 shows the characteristics of volcanite particles in the range of 4.75–8.5 mm in size used in the experiment of deodorization. It should be noted that the relative surface area of granular activated charcoal in the market (with particle size of $4 \sim 8$ mm) is very large, up to 1200 m²/g, and the specific gravity is 0.4 g/mL which is lighter than volcanite.

Fig. 5 shows the results of our study on the ventilation resistance which is a very important problem for the soil deodorization method. The resistance at the entrance per 1m in the packed bed is shown as the height of the water column when the water spraying condition is 0.28 mm/sec and the space velocity of gases is $1.46 \sim 50$ cm/sec. When the granular activated charcoal obtained from the

market (with the particle sizes of $4 \sim 8$ mm) was used and measured, the pressure loss was found to be 100 $mmH_2O^{12)}$ with a space velocity of 15 cm/sec. It is thus observed that the ventilation resistance for charcoal is slightly larger than for the volcanite particles.

It should be pointed out that the ventilation resistance per 1m of soil layer in the current soil deodorization utilizing Ando-soil is $140 \sim 200$ $mmH_2O^{12)}$ provided the space velocity is 5 mm/sec, and the ventilation resistance decreases to a large extent by using grained soil, in which case it is also possible to treat a large volume of odor using a small-sized filter plant.

Table 2　Characteristics of volcanite

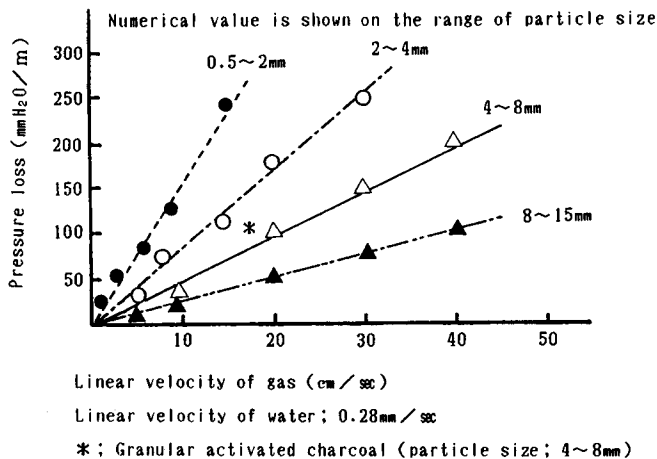| Specific gravity (g/ml) | Bulk specific gravity (g/ml) | Percentage of voids (%) | Specific surface area (m²/g) | Percentage of water (%) | Coefficient of hydrated expansion (%) | Amoung of holding sludge (mg/g-Dry) |
|---|---|---|---|---|---|---|
| 1.62 Average | $0.70 \sim 0.74$ (0.72) | $0.60 \sim 0.67$ (0.62) | $4.71 \sim 5.71$ (5.2) | 29.6 | 135 | $8.00 \sim 8.95$ |

Note;　Particle size: $4.75 \sim 8.5$ mm



Fig. 5　The relationships between pressure loss and linear velocity of gases in the volcanite layer under the water spraying condition.

### 3. Elimination of Hydrogen Sulfide

We have studied the acclimation period and elimination effect of volcanite on hydrogen sulfide from the column experiment.   Fig. 6 shows the outline of experimental equipment employing four glass columns (each with a diametr of 40 mm, and a length of 300 mm) as the elimination layer, and each of them is filled with volcanite particles (3.35～5.6 mm in size) from a gas cylinder.   The sample taken from the gas cylinder (i.e. purified gas) is adjusted to a certain concentration by air dilution in a polyester bag (i.e. fleck sampler[13]).   The following four cases were made in the experiment:

Column 1:   concentration of $H_2S$, 27.5 ppm; ventilation rate, 1.6 cm/sec.
Column 2:   concentration of $H_2S$, 27.1 ppm; ventilation rate, 2.5 cm/sec.
Column 3:   concentration of $H_2S$, 29.1 ppm; ventilation rate, 12.3 cm/sec.
Column 4:   concentration of $H_2S$, 27.0 ppm; ventilation rate, 2.5 cm/sec.

Recycled water (300 mL) was steadily introduced at a rate of 0.16 cm/sec from the upper part of the column so as to replenish the loss of water through
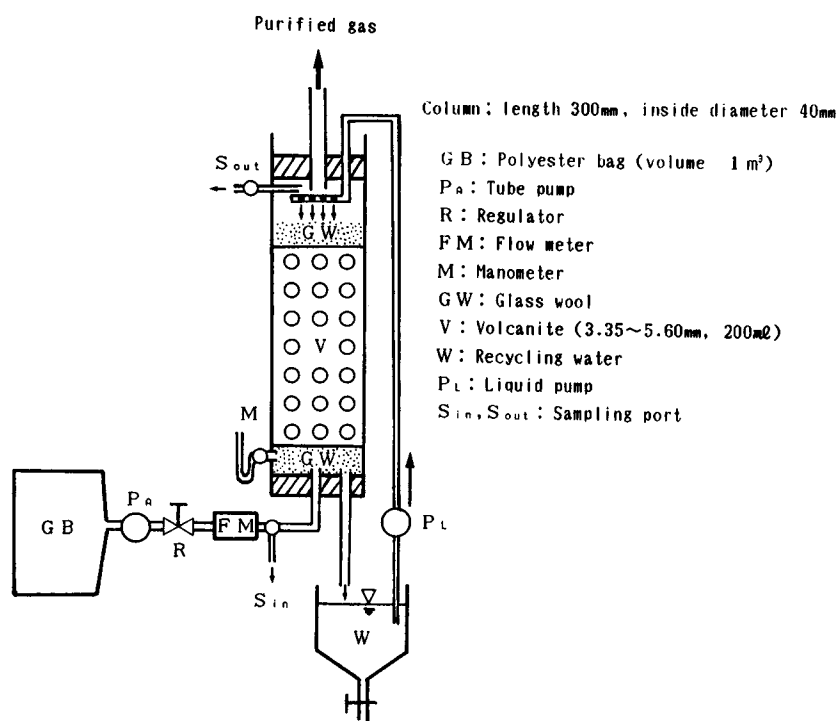


Fig. 6   The schematic outline of experimental equipment.

transpiration during the experiment.    The volcanite particles which had already
been pressure sterilized for three hours in an autoclave at 115°C were put into
column 4 and the ventilation of hydrogen sulfide was carried out.

Before putting the volcanite particles in the column, they were soaked for
12 hours in water discharged from the sewage treatment plant.    This was done
to prevent the blockage of interstitial voids inside the column due to the swelling
of volcanite through absorption of sprinkling water, and also to service the
microorganisms which attach to the surface of particles.

The water discharged from the sewage treatment plant was recycled in order
to supply nutrients to the microorganisms and thus increase their number on the
surface of particles.    The experiment was carried out for 60 days starting from
the ventilation of hydrogen sulfide through the columns.    The concentration of
hydrogen sulfide (measured by GC FPD detector) both at the entrance and at
the exit of the columns and also pH of eater was measured (by electrode method)
during this period.

### 3.1.  *Elimination of Hydrogen Sulfie*

Changes in the elimination ratio of $H_2S$ with the passage of time were
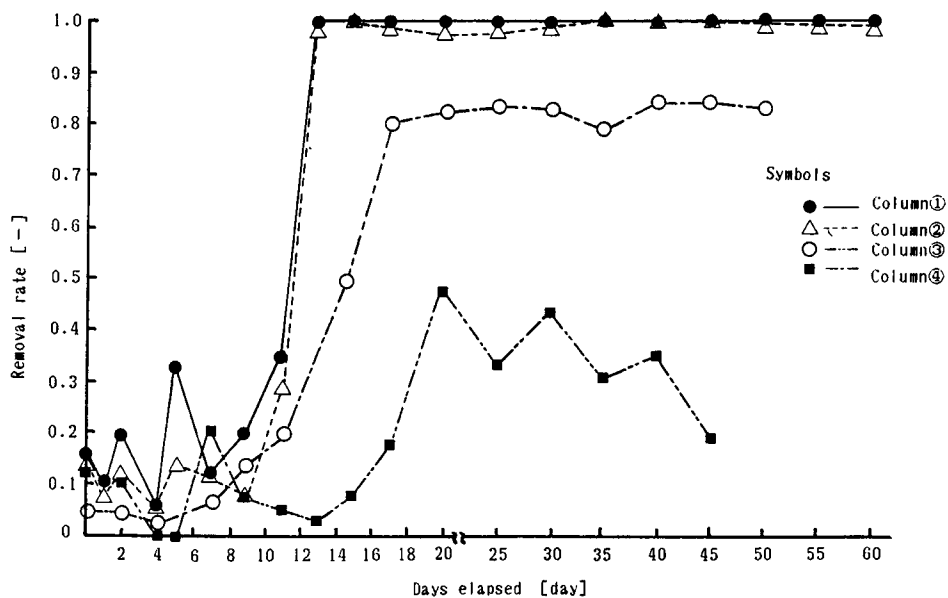measured for different ventilation rates and are plotted in Fig. 7.    In columns 1



Fig. 7   The relationships between the days elapsed and removal rate of
hydrogen sulfide by passing through the volcanite column.

and 2, the elimination ratio during the 10th~11th day after the starting of ventilation was low (below 40%), but it increased rapidly to 100% from around the 12th day onwards, and then $H_2S$ was eliminated almost completely on the 60th day, i.e. the end of the experiment.   It was found that the elimination ratio of $H_2S$ is not significantly affected even if the elimination rate increases to 2.5 cm/sec by graining the soil.   On the contrary, in column 3, the elimination ratio reached almost 80% on the 16th day after the starting of ventilation, and afterward it did not increase until the 50th day.   Furthermore, in the case of the column whose particles of volcanite were once sterilized in an autoclave, the elimination ratio was 10~20% from the starting of ventilation to the second week; afterward, the ratio increased slightly but remained at 30~40% until the 45th day.   The elimination rate in this column was lower compared to other columns.

The residence time of $H_2S$ inside the columns was 6.5~9.4 sec for columns 1 and 2, and 1.2 sec for column 3 which was a relatively shorter time.   It is considered that the residence time (i.e. the difference in the contact time from the biological phase) is directly related to the difference in the elimination ratio, and it is thus necessary to study the contact time and the contact area corresponding to the load.   The contact time of ventilation gas with soil particles is 100 sec[7] which is the standard time for the current soil deodorization method.   In the case of volcanite particles, a contact time of 6~10 sec for 30 ppm concentration of $H_2S$ is necessary to yield sufficient elimination effect.   The contact time is supposed to change according to the type and concentration of odorant which are inherent characteristics of the gas introduced as mentioned previously in the discussion on the elimination mechanism.   This is the subject of a further study from the viewpoint of contact time, as well.

In column 4, the microorganisms which attach to the particles were sterilized in an autoclave at 115°C and high pressure, however, new organisms attach to the particles before being filled into the column through soaking in the water discharged from the sewage treatment plant.   Although this condition is also applied to other columns, the elimination ratio of $H_2S$ is very low even on the 45th day (Fig. 7).   It is probably more related to the interaction between the materials formed inside the layer of biodegradation and the soil components, rather than to the organisms attached to the surface of the soil layer.   In other words, the soil components are altered through treatment at higher temperatures and pressures, which causes a decrease of supplements such as buffer effect and ion exchange.   Besides, since these factors are considered adversely affecting the life-span of soil particles, further study on the behavior of mid-products inside the soil layer and the changes in the soil component is necessary.

The relationship between concentration (C) of $H_2S$ in the packed column and the distance (Z) of passing through the column is given by:

$$C = C\theta \exp\{-(K/V)Z\} \qquad \cdots(3)$$

where $C\theta$ is the concentration at the entrance; $V$ is the linear ventilation rate; and $K$ is a constant.

We substituted the measured values from the columns in the above equation

Table 3    Volume of the constant K

|  | Volcanite (granulated) | Andosoil |
|---|---|---|
| Initial | $1.74 \times 10^{-2}$ | $5.12 \times 10^{-2}$ |
| After acclimation | $7.70 \times 10^{-1}$ | $1.71 \times 10^{-1}$ |

and thus obtained the value of $K$ as shown in Table 3.    The constant $K$ represents the adhesion capacity of $H_2S$ and its dissolution in the packed bed.    It was found that a very high elimination rate is obtained at a stationary state after acclimation, although the initial absorption of grained materials is lower than that of Ando-soil (see Table 3).

### 3.2.    pH value of Recycled Water

The change in the acidity of recycled water with the passage of time, which was measured from the starting of ventilation, is shown in Fig. 8.    The pH values decreased after the 10th day when the acclimation of microorganisms inside the column ended.    The pH value of $1.0 \sim 1.5$ indicates strong acidity around the 60th day.    Compared to the remarks about Fig. 6, the elimination ratio of $H_2S$ remained almost 100% despite the fact that recycled water acquired weaker acidity.    It can therefore be said that the microorganisms involved in the elimination of $H_2S$ are hardly affected by the inhibition of propagation due to the decrease in the pH value of the sprinkling water.    In other words, removal of $H_2S$ in the liquid phase in the soil layer is not controlled by Henry's law but should be explained by some other absorption mechanism.
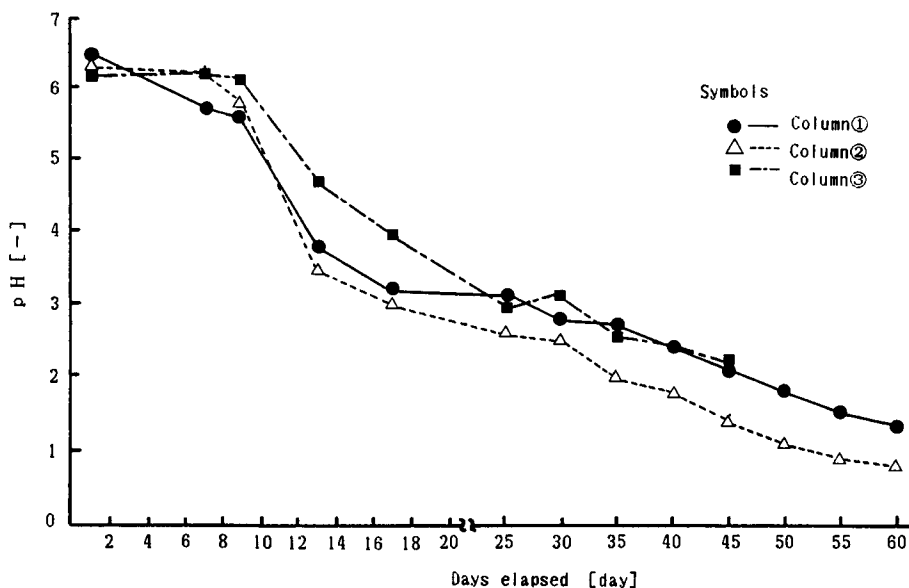
Fig. 8   The relationships between the days elapsed and pH of recycling water
into the volcanite layer.

### 3.3.   *Change in Ventilation Resistance*

Changes in ventilation resistance against the elimination of $H_2S$ with the passage of time were measured for columns 1 and 2 as mentioned in subsection 3.1, and are shown in Fig. 9.   The ventilation resistance in both the columns from the starting day until the 40th day remained around $20 \sim 30$ mm $H_2O$.   Therefore, the resistance increased rapidly and reached 80 mm$H_2O$ on the 60th day when the experiment was stopped because it was assumed that the column had been blockaded by the accumulation of microorganisms.   It was found that the microorganisms accumulated among the particles were removed on the 40th day when the gas ventilation rate was below 2.5 cm/sec.

### 3.4   *Re-sorption Experiment*

The experiment on the elimination of $H_2S$ was repeated after washing out the microorganisms which had blockaded the interstitial voids among particles pushing the tap water upwards in column 1 after the passage of 60 days.   The concentration of $H_2S$ at the entrance was 93.6 ppm, and the conditions of ventilation rate (1.6 cm/sec) and flow rate of recycled water (0.16 cm/sec) were the same as in the previous experiment.   The elimination ratios of $H_2S$ are shown in Fig. 10.   It reached 100% after the 5th day.   However, the ventilation resistance
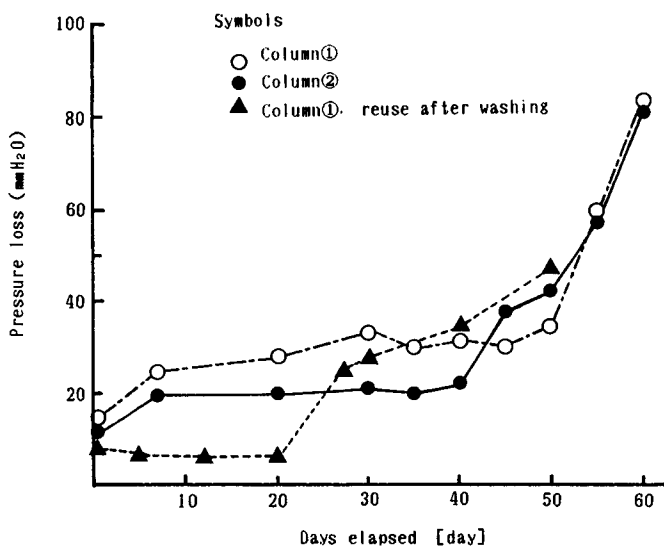
Fig. 9   The relationships between the days elapsed and pressure loss of volcanite column.

increased rapidly from the 40th day, and the tendency to a slight increase in the elimination ratio of $H_2S$ corresponding to this is shown in Fig. 9.   The pH values of the recycled water decreased to $1.0 \sim 2.0$ showing strong acidity which is a similar trend to that in the previous experiment.

The blockage of the column appeared sooner as compared to the first column in the resorption experiment, and this was probably due to an inadequate elimination of microorganisms during the washing of the column or due to the propagation of biological phase.   Further study is required to resolve this matter.

At any rate, it was found that the volcanite employed in this experiment works efficiently as a filter bed which can be used repeatedly by removing the materials accumulated among the particles (i.e. by washing out).   In other words, it is not necessary to change the packed bed of deodorization (as the soil layer is changed in the commonly used method).   The method we propose here is found to be very practical, economical, and efficient.

### 3.5.   *Elimination of Ammonia*

We measured the elimination effect of volcanite against ammonia by the same column experiment employed for hydrogen sulfied.   The glass column (with a diameter of 4 cm, and a length of 30 cm) was filled with 200 ml volcanite with particle sizes of $3.35 \sim 5.6$ mm.
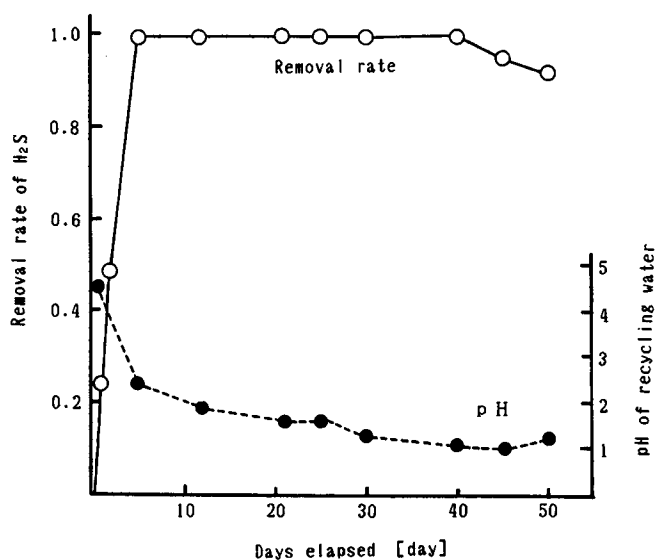
Fig. 10  The relationships between the removal rate of hydrogen sulfide and pH of
recycling water on the reused volcanite column after washing by water

The sample of ammonia gas already adjusted to the concentration of 145 ppm by air dilution was poured in a polyester bag (1 m³), and was sent to the column at a ventilation rate of 7.96 cm/sec for 6.0 min.  The recycled water of the column (20L) was sent at the flow rate of 0.16 cm/sec, and the change in the concentration at the outlet of the column and the pressure loss were measured with the elapse of time.  The volcanite particles were soaked in the aeration tank water of the sewage treatment plant for 12 hours before sending them into the column, and the measurement of ammonia was carried out by tube method detector (manufactured by Komyo Rigaku).

Changes in the elimination ratio with the elapse of time, which were measured for 30 days from the beginning of the experiment, are shown in Fig. 11.  The pH values of recycled water were simultaneously measured, and the ventilation resistance (pressure loss) measured at the entrance of the column are also shown in the figure.  The elimination ratio of ammonia decreased to the minimum on the 4th day, but afterward, it increased with the passage of time and reached the maximum values of 94 ～ 96% on the 20th ～ 25th days, and then declined.  On the other hand, the pH value of recycled water increased gradually up to 8.4 until the 24th day.  When the pH value became 8.8 on the 25th day, the elimination ratio of ammonia tended to decline; it is thus considered that the

acidity of recycled water has an effect on the elimination of ammonia.    Although
the pH value of recycled water showed alkalinity, a large volume of ammonia
was eliminated, and it is considered that the pH buffer action of carbonate
contributes to it.    As regards the ventilation resistance in the column, the increase
of pressure loss was 15 mm $H_2O$ on the 30th day, and no significant blockage
by microorganisms was found, unlike the case of hydrogen sulfide.

### 3.6.  *The Mixed Experiment*

So far the results of experiments have shown that a column filled with
volcanite is effective for removing $H_2S$ and $NH_3$.    We have also carried out an
experiment for the case when both of these odorous gases co-exist.

As the blockage of the column occurred in the previous experiments, for the
mixed experiment, we selected a glass column with inside diameter of 10 cm and
a length of 50 cm, and filled it with 2400 ınL volcanite particles of the size
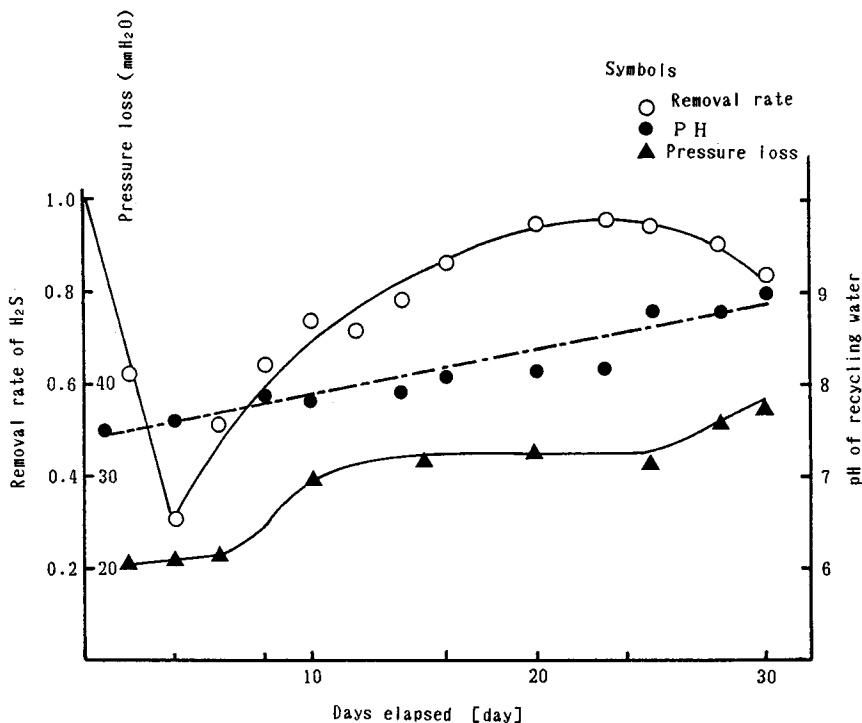4.75 ~ 8.5 mm, and the height of packing was 30 cm.    Volcanite particles were



Fig. 11   The relationships between the days elapsed and removal rate of
ammonia in gas.

Column size; 0.1m i.d×0.5mL
Packed volume of volcanite; 2.4ℓ
Linear velocity of gas; 1.27cm/sec
Recycling water (10ℓ) ; 0.45mℓ/min
Gas concentration;
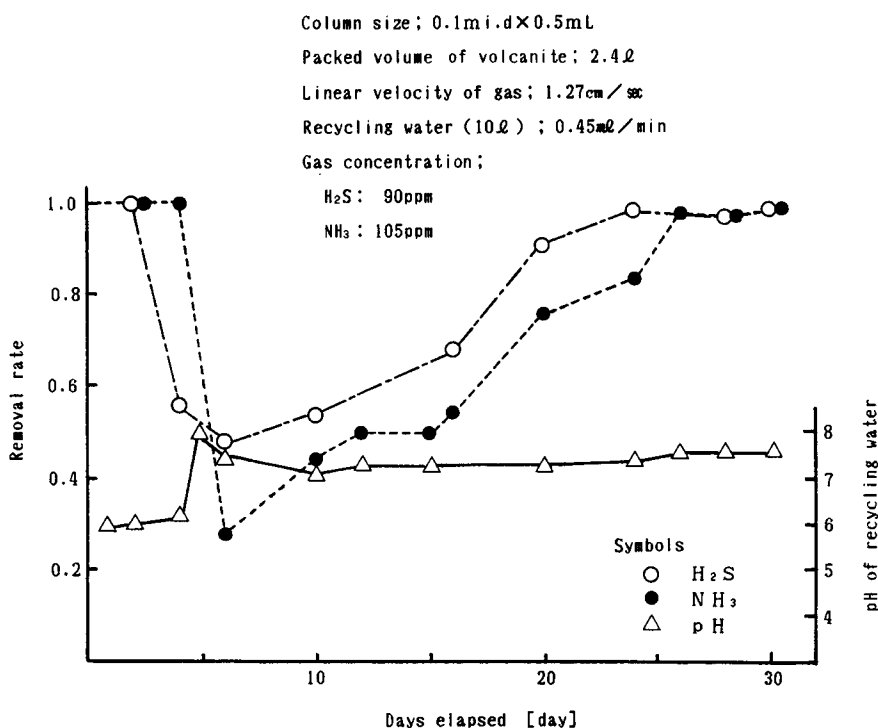  H₂S: 90ppm
  NH₃: 105ppm



Fig. 12   The relationships between the removal rate and the days elapsed
in the case of mixed gases.

soaked in the water of an aeration tank for 12 hours before filling into the column. The flow rate of recycled water (1L) was controlled at 0.45 cm/sec, and the gas ventilation rate at 1.27 cm/sec.

The concentration of $H_2S$ gas was 90 ppm, and that of $NH_3$ was 105 ppm, both of which were adjusted by air dilution in a polyester bag (1 m³) separately. The gases mixed together were sent into the column continuously.

Changes in the elimination ratio of the gases with the elapse of time during the 30 days of the experiment were measured and the results are shown in Fig. 12.

It seems that the physical sorption and absorption to recycled water of both $H_2S$ and $NH_3$ by the volcanite particles was dominant until about the 5th day, but the elimination ratio decreased rapidly around the 6th day when the absorption was saturated and continued so for two weeks. Meanwhile, the propagation of microorganisms, i.e. acclimation in the filter bed inside the column proceeded, and the elimination effect of microorganisms started significantly around the 20th day when the elimination ratios of $H_2S$ and $NH_3$ reached 98~99%.

The pH values of recycled water were consistent with the trend of elimination ratios, and a pH value of 8.0 was reached on the 5th day, but declined to 7.4 from the 6th day onwards due to the formation of sulfuric acid by the biological removal of $H_2S$. The pH value did not increase until the 30th day.

As in the case of elimination of only $NH_3$, when the pH value of recycled water reached 9, and the elimination ratio started declining rapidly; it is supposed that the co-existence of $H_2S$ controls the increase in pH and makes the elimination effect on $HN_3$ last for a longer period.

### 3.7.  Model Experiment in the Field

A model experiment was made on odorous gas (with an odor concentration of $5500 \sim 7300$ folds) in a rendering plant in order to verify the application of the deodorization apparatus utilizing volcanite particles for the elimination of odor

Table 4   Experimental condition

| | | Case A | Case B |
|---|---|---|---|
| Packed tower | i.d. (m) | 0.3 | 0.3 |
| (3 stage) | Height (m) | 0.3 | 0.5 |
| Volcanite | Particle size (mm) | $4.8 \sim 8.5$ | $4.8 \sim 8.5$ |
| | Packed volume (l) | 14 | 25 |
| | Height of layer (cm) | 20 | 35 |
| Recycling water | Flow rate (l/min) | 6 | 6 |
| | Linear velocity in the Packed layer (cm/sec) | 0.14 | 0.14 |
| Test gas | Flow rate ($m^3/h$) | 12.7 | 38.1 |
| | Linear velocity in the Packed layer (cm/sec) | 5 | 15 |
| Concentration of | $NH_3$ (ppm) | 380 | 480 |
| odorants | TMA (ppm) | 40 | 40 |
| (average) | $H_2S$ (ppm) | 90 | 90 |
| | MM (ppm) | 50 | 40 |
| Odor concentration | fold | $5,500 \sim 7,300$ | $5,500 \sim 7,300$ |
| Temperature of gas | °C | $38 \sim 41$ | $38 \sim 41$ |

in an actual field, and we studied the conditions of design and the operation factors of the method.

The outline of equipment employed and experimental conditions are presented in Table 4. The three stages of polyvinyl chloride pipes in two different sizes (namely, case A with an inside diameter of 30 cm and a length of 30 cm, and case B with an inside diameter of 30 cm and a length of 50 cm) were connected to each other by a flange in each packed layer, and volcanite particles (4.7~8.5 mm in particle size) were filled in each stage: 20 cm for case A, and 35 cm for case B. The sprinkling of recycled water was adjusted at 0.14 cm/sec of linear velocity in the filter layer, and the volume of odorous gas introduced was 12.7 $m^3$/h (LV=5 cm/sec) for experiment A, and 38.1 $m^3$/h (LV=15 cm/sec) for experiment B.

The concentration of odorous gases changed slightly due to variation of work process in the factory, and the degree of change for each material was in the range of $\pm 20\%$ of the values given in Fig. 4. In the same way, the odor concentrations of emitted gas were 5,500~7,300 fold.

Changes in the elimination of each material (i.e., $NH_3$, TMA, $H_2S$, and MM) were measured. Before starting the experiment, about 20 L of the water
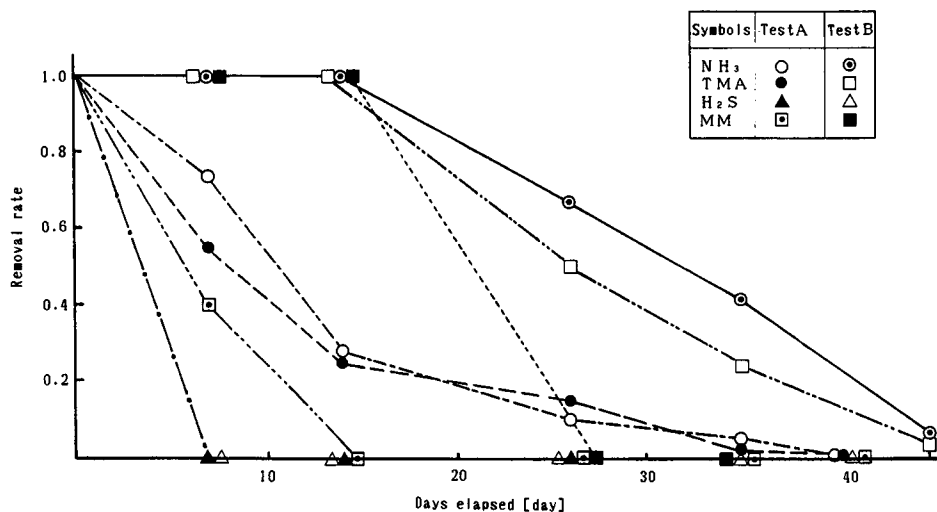


Fig. 13   The results of field tests, the relationships between the removal rate of odorants in the gases from N-rendering plant and the days elapsed.

of the aeration tank in the factory was sprinkled and recycled from the upper part of the filter layer, then acclimatization was carried out for ten days, and after this, the odorous gas was introduced.   The measurements were made continuously for 45 days.   Fig. 13 show the results of this field experiment.   It can be seen that the concentration of each material decreased rapidly after acclimatizing the water for 8 days in experiment A, and for 14 days in experiment B.   The elimination ratio of each material was more than 90% for 25 days in experiment A.   However, $H_2S$ was eliminated almost completely on the 8th day in experiment B., and the removal of MM also reached nearly 100% on the 25th day and afterward.   On the contrary, the elimination ratios of $NH_3$ and TMA barely reached 90% on the 45th day.   It is probably due to the decrease in the elimination ratio of N group materials because the pH value of recycled water was not
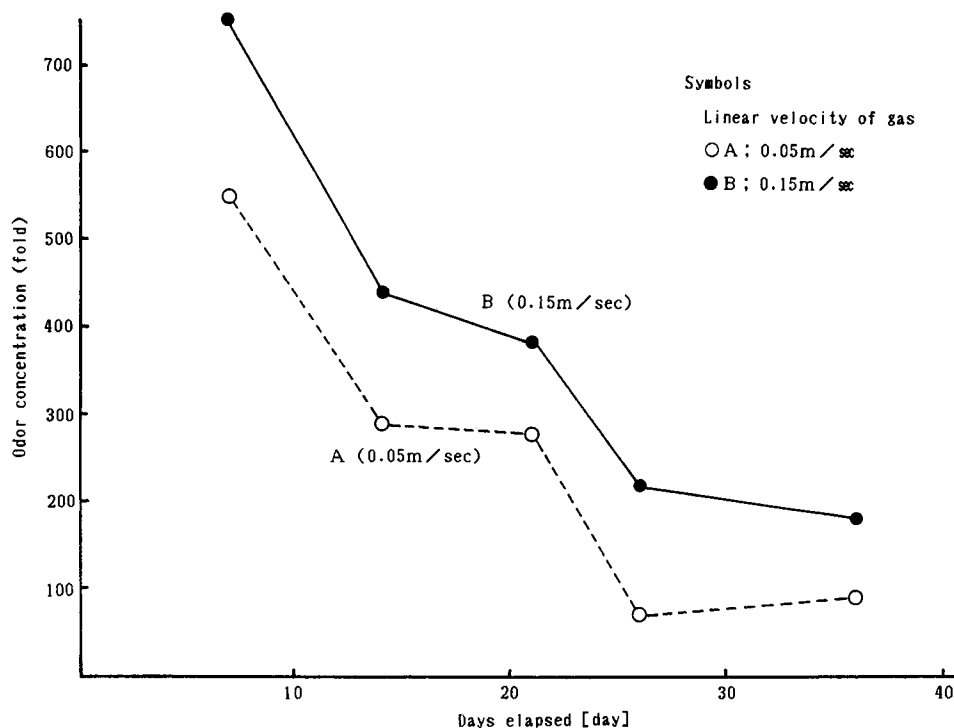
Fig. 14   The relationships between odor concentration of treated gas and the days elapsed, in the case of N-rendering plant, source gas odor concentration of source gas in 5,500~7,300 (fold).

adjusted, and the experiment was thus repeated. According to this 30-day long experiment, the elimination ratios of $NH_3$ and TMA reached almost 100% on the 20th day by maintaining the pH value of recycled water around $6.8 \sim 7.2$.

Changes in odor concentration with the passage of time, which were measured at the outlet of the packed layer, are shown in Fig. 14. The odor concentration of the gas (which was $5,500 \sim 7,300$ fold at the entrance) was $70 \sim 90$ fold in experiment A and $180 \sim 220$ fold in experiment B after 25 days, both of which show significant decrease. This deodorization system was found to be very effective to decrease the odor concentration and remove the odorous gases in the rendering plant. In these series of experiments, we obtained satisfactory results of the conditions for a deodorization mechanism which we had studied. Moreover, the remarks made here about the time of washout of the packed layer are useful for practical purposes and another experiment on this effect is currently being carried out.

## Conclusions

The complaints about stinking gases emitted from factories have increased and so much expanded that emission of odorous gases is now a major environmental problem, since people have become environmentally conscious, demanding a comfortable environment. For this reason, measures against odor are likely to intensify not only towards deccreasing odor concentration and eliminating odorous gases but also towards creating an environment filled with fragrance.

On the other hand, technical development of the common measures against odor emission from industrial plants is necessary to to achieve resource and energy conservation, high efficiency of equipment and low cost. There are also several more specific problems to be solved such as measures against certain emission sources of odor which have no outlet, measures against background odor of low concentration, and the development of effective methods and equipment to combat odorous gases produced by small-scale industries. Various systems are suggested in this regard.

The method of biological deodorization has drawn attention owing to its several merits such as treatment of large amounts of mixed gases which is a characteristic of odor phenomenon, flexibility against variation in the quality and volume of the load, and relatively low costs of treatment. The utilization of this method is expanding in many fields with innovations drawn from the experience of each field.

Among the methods of biological deodorization, the deodorization method

utilizing soil as the filter layer is widely employed because it is effective for the removal or diminishing of odorants, owing to certain characteristics of soil, i.e. adhesion of microorganisms, an environment for propagation, or buffer action, and exchangeability.

However, there are several problems which prevent expansion in the applications of the soil deodorization method; such problems include large ventilation resistance in the soil layer, requirement of a large filter area, occurrence of secondary products and consolidation, blocking of soil due to its water retaining power, exchange of soil layer, and unstable design of apparatus due to less known elimination mechanism.

In this paper, we experimentally concluded that by graining the soil to decrease the filter area and by increasing the ventilation rate to $0.3 \sim 0.5$ m/sec of the soil layer, adequate capacity is obtained for the elimination of odorants.  This high efficiency for the elimination of odorous gases and the practical usefulness of the method we proposed here were shown by the results of experiments on columns filled with volcanite particles ($4.7 \sim 8.5$ mm in size) in the lab as well as in the field using a small-scale model experiment on the elimination of odorous gases emitted from a rendering plant.

At present, we are proceeding with a study on modeling of the elimination mechanism of odorants based on the experiments presented in this paper; we are also examining measures against mixed odorous materials which have different biochemical properties.

## Acknowledgements

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