

Absorption of Ammonia Gas from a Composting Plant using Carbonated Water

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Odors from composting plants are a serious public nuisance. Ammonia gas (NH₃) is the main molecule responsible for bad odors that arise from composting of organic wastes such as animal manure. Carbon dioxide (CO₂) is known to increase the solubility of NH₃ in water. Taking that effect of CO₂ into account, numerical calculation of the absorption of NH₃ into water was carried out under the assumption of quasi-equilibrium conditions. Based on that theoretical consideration, the authors propose a new deodorizing process that consists of a carbonator and a reactor. The carbonated water produced by pressurized CO₂ gas is transported to the reactor, where NH₃ gas dissolves efficiently in the water. Carbonated water with NH₃ is useful as a liquid fertilizer.

It is expected that the consumption of water in the new process is significantly lessened compared to that consumed in traditional processing. According to theoretical considerations, 100 ppm NH₃ in 1 m³ air can be reduced to 10 ppm after deodorization using 0.1 kg carbonated water at CO₂ concentration of 2 × 10⁻³ kg L⁻¹.

Key Words : Deodorization, Ammonia, Carbon dioxide, Carbonated water, Thermal equilibrium

1 INTRODUCTION

Soil degradation is a critical issue globally. Intensive agriculture reduces soil organic matter content and alters aggregate stability. The addition of chemical fertilizers is a conventional practice to inject nutritive substances into soil. In many cropping areas where breeding activity has disappeared, a shortage of organic matter sources exists.

Organic farming presents an alternative to conventional farming systems, with the potential to enhance agricultural sustainability and food quality [1]. The composting of organic wastes stabilizes the constituent organic matter. The observed effects on aggregate stability depend on the characteristics of both exogenous organic matter and soil [2]. Recent revision of the required quality standards [3] is expected to enhance the production of high-quality compost which increase the organic-matter contents of the soils and improve their physical properties. Organic wastes offer a great resource for use in compost production. Animal manure compost can be a useful amendment to arable crop lands. Therefore the number of compost producers and the amount of compost are increasing in Japan [4].

Unfortunately, odors from composting plants pose a serious public nuisance. Complaints against odors have led to composting plant closures [5]. To suppress the odors, composting plants are usually equipped with deodorizing systems such as a water scrubber, a biofilter, or an ozonator. Among odor-causing contaminants, NH₃ gas is the main molecule responsible for bad odors that arise from composting of animal manure.

A biofiltration is cheap system and generates no wastewater, but deodorizing reaction occurs too slowly to treat large amount of gas. An ozonation is clean system, but large amount of ozone gas is required for an effective deodorization and its production cost is expensive. Water scrubbing is not an effective method for deodorization. Water scrubbing is also inefficient treatment for deodorization since solubility of NH₃ is small. To increase its solubility, chemical scrubbing has been used, using strong acid such as sulfuric acid. However, managements of wastewater and operation control are required strictly. Corrosion of the equipment is another severe problem. Therefore this treatment has not been popular [6].

Considering that the carbonated water with NH₃ could be used as a liquid fertilizer, the authors propose the new deodorizing

process using CO₂ instead of strong acid. In this treatment, strict operation control is easy and corrosion damage is severe. Few studies have been done on the deodorization using CO₂. In this paper, the influence of CO₂ on the absorption of NH₃ into water is theoretically investigated based on a simple quasi-equilibrium model.

2 BASIC RELATIONS

2.1 Equilibrium absorption of NH₃ in NH₃-CO₂-water system

In this section, the authors consider the equilibrium concentrations of NH₃ and NH₄⁺ in water.

Figure 1 illustrates equilibrium relations in a NH₃-CO₂-water system. The concentrations of undissociated NH₃ and CO₂ in water are represented respectively by [NH₄OH] and [H₂CO₃]. In an aqueous phase, NH₃ and CO₂ molecules exist as NH₄OH and H₂CO₃; ammonium ion and hydrogencarbonate ion are dissociated, respectively, from NH₃ and CO₂ molecules as NH₄⁺ and HCO₃⁻. The concentration of carbonate ion, [CO₃²⁻] is negligibly small as dissociation constant of HCO₃⁻ to CO₃²⁻ [7] is four orders of magnitude smaller than that of H₂CO₃ to HCO₃⁻. Equilibrium relations are governed by the following six equations.

Henry's laws for NH₃ and for CO₂ are expressed respectively in the forms of **Eqs. (1) and (2)**.

$$(P_N) = H_N[\text{NH}_4\text{OH}], \text{ and} \quad (1)$$

$$(P_C) = H_C[\text{H}_2\text{CO}_3]. \quad (2)$$

In the above equations, (P_N) and (P_C) represent the partial pressures of NH₃ and CO₂, respectively; the Henry's law constants for NH₃ and CO₂ are denoted respectively as H_N and H_C.

The dissociation equilibria in the aqueous phase are expressed as **Eqs. (3)-(5)**.

$$\frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_4\text{OH}]} = K_N, \quad (3)$$

$$\frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = K_C, \quad (4)$$

$$[\text{H}^+][\text{OH}^-] = K_W. \quad (5)$$

Here, [NH₄⁺], [OH⁻], [H⁺], and [HCO₃⁻] respectively represent concentrations of NH₄⁺, OH⁻, H⁺, and HCO₃⁻ in water. The dissociation constants of NH₃, CO₂, and water are expressed respectively as K_N, K_C, and K_W.

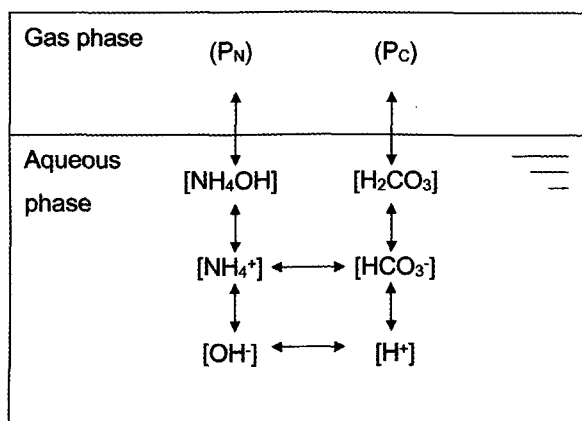


Figure 1 Equilibrium relations in a NH₃-CO₂-water system.

The electro-neutrality rule is described as **Eq. (6)**.

$$[\text{NH}_4^+] + [\text{H}^+] = [\text{HCO}_3^-] + [\text{OH}^-]. \quad (6)$$

If the total ammonium concentration in aqueous phase is defined as [N_T]. It is expressed as

$$[\text{N}_T] = [\text{NH}_4\text{OH}] + [\text{NH}_4^+]. \quad (7)$$

By solving **Eqs. (1)-(6)**, [N_T] is written as

$$[\text{N}_T] = \frac{(P_N)}{H_N} \left(1 + \frac{K_N}{K_W} [\text{H}^+] \right), \quad (8)$$

where [H⁺] is

$$[\text{H}^+] = \sqrt{\frac{H_N K_W \{H_C K_W + K_C (P_C)\}}{H_C \{H_N K_W + K_N (P_N)\}}}. \quad (9)$$

Equations (8) and (9) show that the presence of CO₂ increases the solubility of NH₃.

2.2 Removal of NH₃ gas in NH₃-CO₂-air mixture by water

In the previous section, it was shown clearly that the addition of CO₂ gas enhances the absorption of NH₃ into water.

Based on consideration in section 2.1, a deodorizing process shown in **Figure 2** is proposed, by which the gas flow of NH₃-CO₂-air mixture encounters the water flow and travels in the same direction at the same velocity in the reactor. Gaseous NH₃ and CO₂ are absorbed into water. Consequently, the concentration of NH₃ in the gas phase decreases and the total ammonia in the water increases. Finally, both concentrations achieve certain equilibrium values. Subscripts of _i, _o denote initial values.

Removal efficiency of NH₃ in this process will be discussed as a function of specific consumption of water and CO₂.

The initial concentration of NH₃ in the water is assumed to be zero. The final total ammonia concentration, [N_T]_o, depends on the flow rate of the gas mixture, Q, that of the water, M, and the final partial pressure of CO₂, (P_C)_o.

The law of mass conservation for ammonia species provides the following relation:

$$\frac{(P_N)_i Q}{RT} = \frac{(P_N)_o Q}{RT} + M[\text{N}_T]_o, \quad (10)$$

where R and T respectively represent a universal gas constant and temperature.

If removal efficiency, η is defined as **Eq. (11)**

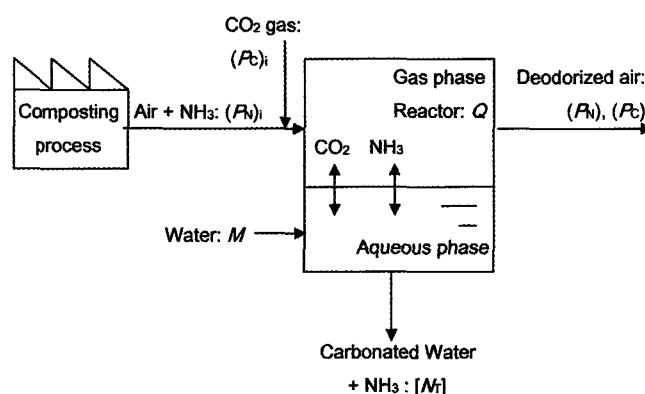


Figure 2 Schematic illustration of the removal of NH₃ from a NH₃-CO₂-air mixture using water

$$\eta = \frac{(P_N)}{(P_N)_i} \quad (11)$$

Substituting Eqs. (8), (9) and (11) into Eq. (10) engenders Eq. (12):

$$\frac{M}{Q} = \frac{H_N K_w (1 - \eta)}{RT \eta (K_w + K_N [H^+])}, \quad (12)$$

where

$$[H^+] = \sqrt{\frac{H_N K_w \{H_C K_w + K_C (P_C)_i\}}{H_C \{H_N K_w + K_N \eta (P_N)_i\}}}. \quad (13)$$

A similar relation of Eq. (10) should be satisfied for CO₂.

$$\frac{(P_C)_i Q}{RT} = \frac{(P_C) Q}{RT} + M [C_T], \quad (14)$$

In Eq. (14) above, (P_C)_i and [C_T] respectively denote the initial partial pressure of CO₂ and concentration of total CO₂ in aqueous phase.

The quantity of CO₂ in aqueous phase is negligibly small; it is much less than that in gas phase for practical deodorization. Accordingly, (P_C) is approximated by Eq. (15)

$$(P_C) \approx (P_C)_i \quad (15)$$

Therefore Eq. (9) can be rewritten in terms of (P_C)_i and (P_N)_i as

$$[H^+] = \sqrt{\frac{H_N K_w \{H_C K_w + K_C (P_C)_i\}}{H_C \{H_N K_w + K_N \eta (P_N)_i\}}}. \quad (16)$$

From Eq. (16), the specific consumption of water, Eq. (12) is defined as a function of (P_C)_i, (P_N)_i and η .

Furthermore, related to CO₂ consumption, m_c is written using Eqs. (14) and (15).

$$m_c = \frac{(P_C)_i Q}{RT} \quad (17)$$

Substituting Eq. (17) into (16) obtains Eq. (18):

$$[H^+] = \sqrt{\frac{H_N K_w \left(H_C K_w + K_C RT \frac{m_c}{Q} \right)}{H_C \{H_N K_w + K_N \eta (P_N)_i\}}}, \quad (18)$$

where m_c Q⁻¹ represents specific consumption of CO₂. Therefore, specific consumption of water, Eq. (12) is defined as a function of m_c Q⁻¹ and η (P_N)_i.

2.3 Quasi-equilibrium absorption of NH₃ in a NH₃-carbonated water system

As you will know in numerical calculations (see Figure 10), huge amounts of CO₂ consumption are required for the previous process because CO₂ solubility in water is small. Therefore, it is rather difficult to apply this process to practical deodorization. The use of carbonated water is considered in this section to overcome this disadvantage.

Henry's law and dissociation equilibria of CO₂ are represented respectively following Eqs. (12) and (13).

$$[H_2CO_3]_i = \frac{(P_C)_i}{H_C}, \quad (19)$$

and

$$\frac{[H^+][HCO_3^-]_i}{[H_2CO_3]_i} = K_C, \quad (20)$$

where subscripts []_i denote the initial value. The gas mixture of NH₃-air is absorbed in the carbonated water with initial concentration of [H₂CO₃]_i.

Henry's law and the dissociation equilibrium for NH₃ are represented respectively by Eq. (21) and Eq. (22).

$$(P_N) = H_N [NH_4OH] \quad (21)$$

$$\frac{[NH_4^+][OH^-]}{[NH_4OH]} = K_N \quad (22)$$

The rate of NH₃ absorption by carbonated water might be greater than that of CO₂ desorption from carbonated water. No transfer of CO₂ from carbonated water to the gas phase is assumed. The sum of [H₂CO₃] and [HCO₃⁻] is constant. Therefore, increase of [HCO₃⁻] results in decrease of [H₂CO₃]. Equation (4) is modified as

$$\frac{[H^+]([HCO_3^-]_i + y)}{[H_2CO_3]_i - y} = K_C, \quad (23)$$

where y represents the increase of [HCO₃⁻] attributable to the absorption of NH₃ into carbonated water.

The relation on the dissociation of water is in the same form as

$$[H^+][OH^-] = K_w. \quad (24)$$

The relation of electro-neutrality is expressed as

$$[NH_4^+] + [H^+] = [HCO_3^-]_i + y + [OH^-]. \quad (25)$$

Solving the simultaneous equations of Eqs. (21)-(25), total ammonia concentration, [N_T] is written in the following form:

$$[N_T] = \frac{(P_N)}{H_N} \left[1 + \frac{K_N}{K_w} \left\{ 2 \sqrt{-\frac{a}{3}} \cdot \cos \left(\frac{\theta}{3} \right) - \frac{K_C}{3} \right\} \right], \quad (26)$$

where

$$\cos \theta = -\sqrt{\frac{b^2}{4} \div \left(-\frac{a^3}{27} \right)},$$

$$a = \frac{1}{3} (3p - K_C^2),$$

$$b = \frac{1}{27} (2K_C^3 - 9K_C p + 27q), \quad (27)$$

$$p = -\frac{H_N K_C K_w \{ (P_C)^* + \sqrt{H_C K_C (P_C)^*} \} + K_w^2 H_C K_N}{H_C \{ H_N K_w + K_N (P_N) \}}$$

and

$$q = -\frac{K_w^2 H_N K_C}{H_N K_w + K_N (P_N)}.$$

Therein, (P_C)^{*} is defined as the partial pressure of CO₂ gas equilibrated with the concentration of [H₂CO₃]_i.

2.4 Removal of NH₃ gas from an NH₃-air mixture using carbonated water

Different from previous CO₂ gas processing, carbonated water reacts directly with NH₃ in air. A carbonator is installed separately outside the reactor for NH₃ absorption, as shown in Figure 3.

In the similar manner to that used in section 2.3, specific consumption of carbonated water is obtained by substituting Eq. (11) into Eq. (10),

$$\frac{M}{Q} = \frac{(P_N)_i(1-\eta)}{RT[N_T]} \quad (28)$$

where $[N_T]$ is given by Eqs. (26) and (27). Replacing (P_N) by $\eta(P_N)_i$, Eq. (26) and p and q in Eq. (27) are written as

$$[N_T] = \frac{\eta(P_N)_i}{H_N} \left[1 + \frac{K_N}{K_W} \left\{ 2\sqrt{\frac{a}{3}} \cdot \cos\left(\frac{\theta}{3}\right) - \frac{K_C}{3} \right\} \right]$$

$$p = -\frac{H_N K_C K_W \left\{ (P_C)^* + \sqrt{H_C K_C (P_C)^*} \right\} + K_W^2 H_C H_N}{H_C \{ H_N K_W + K_N \eta (P_N)_i \}} \quad (29)$$

and

$$q = -\frac{K_W^2 H_N K_C}{H_N K_W + K_N \eta (P_N)_i}$$

Similarly, Eq. (28) is defined as a function of $\eta(P_N)_i$ and $(P_C)^*$.

The specific consumption of CO_2 , $m_c Q^{-1}$ is given approximately as Eq. (30).

$$\frac{m_c}{Q} = \frac{M(P_C)^*}{QH_C} \quad (30)$$

Therefore Eq. (28) is defined as a function of $m_c Q^{-1}$ and $\eta(P_N)_i$.

3 NUMERICAL CALCULATION

3.1 Numerical relation of NH_3 in NH_3-CO_2 -water

Numerical calculations for Eqs. (8) and (9) are carried out using the following constants at 298 K: $H_C = 1.66 \times 10^3 \text{ Pa L mol}^{-1}$; $H_N = 2.90 \times 10^6 \text{ Pa L mol}^{-1}$; $K_N = 1.76 \times 10^{-5}$; $K_C = 1.76 \times 10^{-3}$; $K_N = 4.38 \times 10^{-7}$; and $K_W = 1.00 \times 10^{-14}$ (Edwards, 1978). The relation between (P_N) and $[N_T]$ is illustrated in Figure 4 for various (P_C) , 0, 10, 10^2 , 10^3 , 10^4 and 10^5 Pa. The increase of CO_2 gas pressure increases the total ammonia concentration, as described in section 2.2.

3.2 Numerical results of removal of NH_3 from a NH_3-CO_2 -air mixture using water

Figure 5 shows the variation of NH_3 removal efficiency in NH_3-CO_2 -air mixture with specific water consumption for various (P_C) , 0, 10, 10^2 , 10^3 , and 10^4 Pa at 298 K. The initial concentration of NH_3 gas, $(P_N)_i$, is assumed to be 10 Pa.

From Figure 5, it is known that the increase of the CO_2 volume ratio from 0 to 0.1 decreases the specific water consumption from 5 to 0.1 kg m^{-3} -air for the NH_3 reduction of $\eta = 0.1$.

Figure 6 shows the variation of specific water consumption

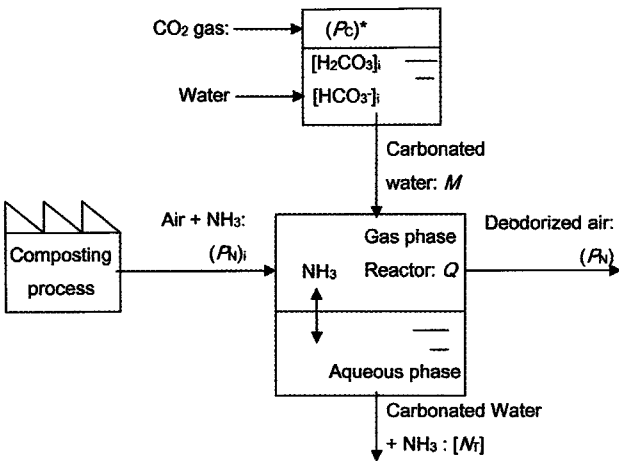


Figure 3 Schematic illustration of the removal of NH_3 using carbonated water

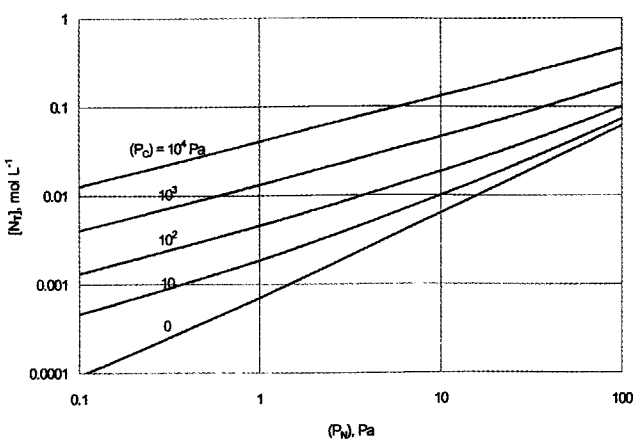


Figure 4 Equilibrium relations between (P_N) and $[N_T]$ for various (P_C) at 298 K

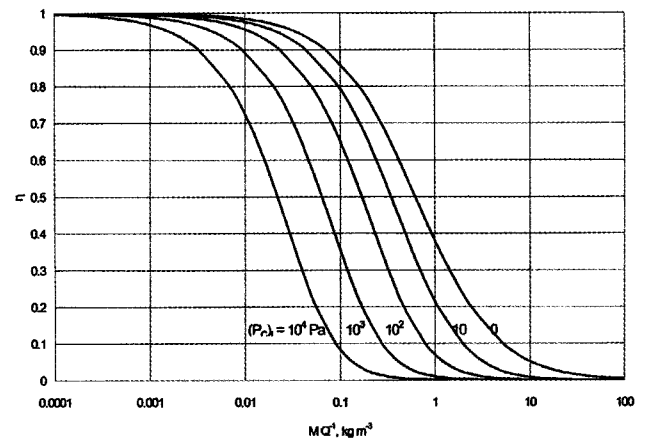


Figure 5 The variations of NH_3 removal efficiency in NH_3-CO_2 -air mixture with specific water consumption for various CO_2 pressures. The initial concentration of NH_3 gas, $(P_N)_i$ is 10 Pa.

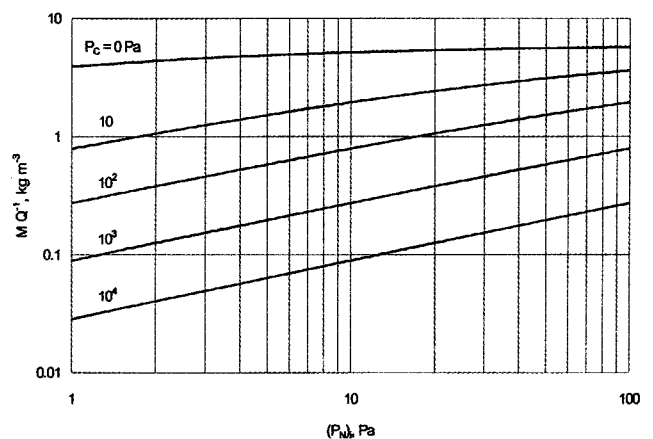


Figure 6 Variations of specific water consumption with initial partial pressure of NH_3 for various CO_2 pressures in NH_3-CO_2 -air mixture. The NH_3 removal efficiency, η , is 0.1.

with initial partial pressure of NH_3 in a NH_3 - CO_2 -air mixture for various CO_2 pressures at 298 K. The NH_3 removal efficiency, η , is assumed as 0.1.

3.3 Numerical relation in NH_3 -carbonated water system

Numerical results of Eq. (26) are shown as a function of (P_N) for various $(P_C)^*$ in Figure 7. The effect of CO_2 on the solubility of NH_3 increases with decreased (P_N) , as shown in Figure 7.

3.4 Numerical results on removal of NH_3 gas in NH_3 -air mixture using carbonated water

Figure 8 shows the variation of NH_3 removal efficiency with specific carbonated water consumption for various $(P_C)^*$ in an NH_3 -air mixture. Their relations were obtained by computing Eq. (28) at $(P_N)_i = 10$ Pa.

From Figure 8, it is known that the specific consumption of water is nearly equivalent to that in the CO_2 gas process if the carbonated water is saturated by CO_2 at the pressure of 10^5 Pa.

Figure 9 shows the variation of specific carbonated water consumption with initial partial pressure of NH_3 in an NH_3 -air mixture for various pressurized carbonated water at 298 K. The NH_3 removal efficiency, η is assumed as 0.1.

Figure 10 shows a comparison of specific CO_2 consumption between CO_2 gas process and carbonated water one, at reduction rate of $\eta = 0.1$, the relation of $m_c Q^{-1}$ and MQ^{-1} for both cases.

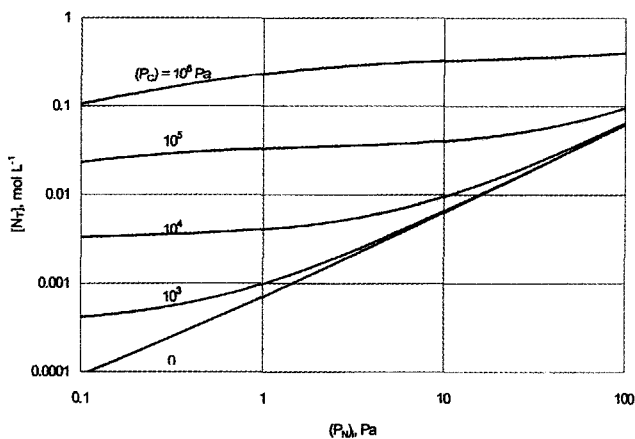


Figure 7 Relation between (P_N) and $[\text{N}_T]$ in carbonated water at 298 K.

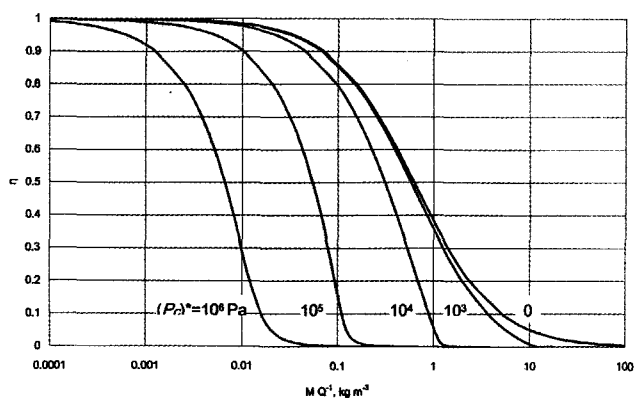


Figure 8 Reduction of NH_3 in air as the function of specific consumption of carbonated water at 298 K.

The value of $m_c Q^{-1}$ for CO_2 gas processing is calculated using Eqs. (12)-(18); that for carbonated water processing is shown by Eqs. (28)-(30).

The consumption of CO_2 for carbonated water processing, $m_c Q^{-1}$ is estimated as $2 \times 10^{-4} \text{ kg m}^{-3}\text{-air}$, which is three orders of magnitude less than that for CO_2 gas processing.

4 CONCLUSION

Taking into account that acid enhances absorption of NH_3 into water, the authors carried out the theoretical simulation on the removal of NH_3 from odorous air using CO_2 .

NH_3 removal rate was obtained by solving following the 8 equations simultaneously; two Henry's laws for NH_3 and CO_2 , three dissociation equilibria for ammonia, carbon dioxide and water, a electro-neutrality among ions in aqueous solution and two laws of mass conservation for ammonia and carbon dioxide.

In the CO_2 gas process, the addition of CO_2 in air results in the reduction of water consumption. Without CO_2 , specific water consumption of $5 \text{ kg m}^{-3}\text{-air}$ is required to remove NH_3 from 10 Pa to 1 Pa. Numerical calculation revealed that the addition of 10% volume to the air reduce the water consumption by one fiftieth

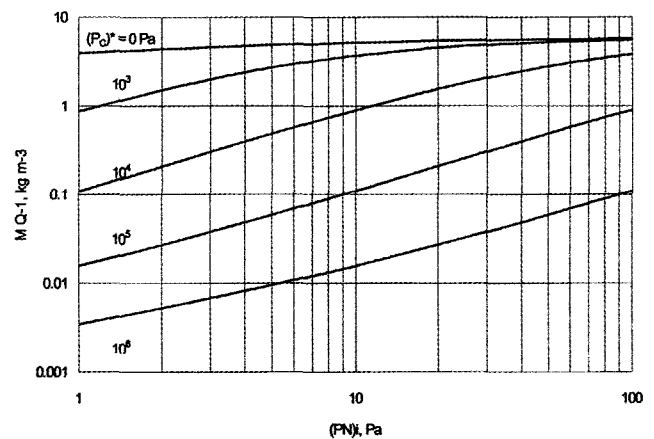


Figure 9 Variations of specific carbonated water consumption with initial partial pressure of NH_3 for various $(P_C)^*$ in NH_3 -air mixture. The NH_3 removal efficiency, η , is 0.1.

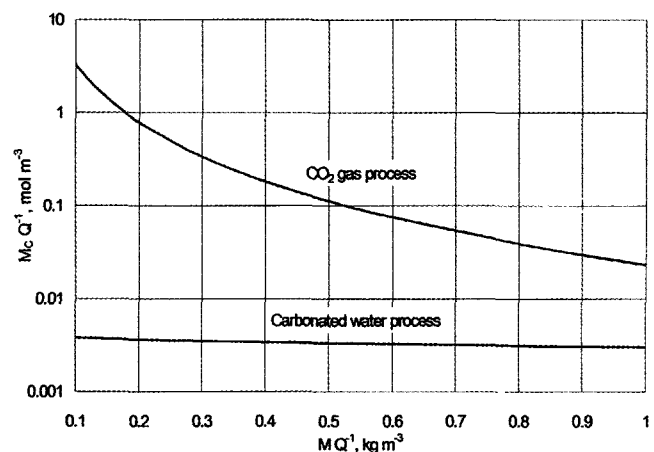


Figure 10 Comparison of specific CO_2 consumption between CO_2 gas processing and carbonated water processing

compared to that without CO₂.

In the carbonated water process, not only water consumption but also CO₂ consumption can be reduced. If the water is saturated by 10⁵ Pa-CO₂ in a carbonator, water consumption is almost equal but CO₂ consumption can be reduced to 1/1000, compared to those of CO₂ gas process.

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NOMENCLATURE

- [] Concentration in aqueous phase
H Henry's law constant
K Dissociation constant
N Total ammonia concentration in aqueous phase
M Flow rate of water
m Gas consumption of mol.
(*P*) Partial pressure of NH₃
Q Flow rate of gas
R Universal gas constant
T Temperature
y Increase of HCO₃⁻

Greek symbols

- η* removal efficiency

Subscripts

- C CO₂
i Initial value
N NH₃
T Total concentration in aqueous phase
W Water

Superscript

- * Partial pressure in carbonator

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