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Removal of Deposits and Improvement of Shelf Life in CO_2-Rich Mineral Water by Ozone-Microbubbles

Un Hwa Choe, Jong Hyon Choe, Yong Jun Kim

***Abstract*—**The aim of this study was to effectively remove Fe^{2+} by using ozone microbubbles in bottled mineral water to prevent sediment from occurring during storage and increase shelf life. By considering the characteristics of mineral water with low solubility of ozone and high CO_2 content, a suitable ozone injection step was chosen and a mineral water treatment method using microbubbles was proposed. As a result of the treatment of the bottled mineral water with ozone microbubbles, the iron ion concentration was reduced from 0.14 mg/L to 0.01 mg/L, and the shelf life increased to 360 days. During the treatment, the concentrations of K^+ and Na^+ were almost unchanged, and the deposition time was reduced to one-third compared to the natural oxidation.

***Keywords*—**CO_2–rich mineral water, ozone-micro bubble, shelf life, bottled mineral water, water treatment.

I. Introduction

THE mineral waters have been widely used since long ago because of its abundance of natural minerals useful for human life. In recent years, the variety and production of bottled mineral waters have increased rapidly due to water pollution resulting from various causes, depletion of drinking water sources and increasing human demand for health. An important issue in the production of bottled mineral water is that the physical and chemical characteristics, including hygienic safety and color and taste after bottle packaging, are not changed for a period of time. Therefore, studies were conducted to analyze the microbial status of bottled mineral water and to determine the cause of microbial development and growth, and to conclude that the bottling and storage process of mineral water affects the quantity and quality of microorganisms [1]-[4].

It is not only microorganisms that affect the quality of mineral water. In mineral water, unstable components such as iron, manganese, and sulfur are also present, which are allowed to be removed for these components [5]. Also, according to EU directive 2003/40/EC, it is possible to use ozone-rich gases for the treatment of natural mineral water containing carbon dioxide [6]. The results of the study show that limited treatment of filtration, oxidation, precipitation and ozone treatment should be performed so that the physicochemical properties of mineral waters along with microorganisms are not changed during the bottling process. The use of ozone gas in water treatment began about a century ago and was used to purify the dirty water by microorganisms [7]. Later, chlorine and chlorine dioxide were used to effectively treat contaminants, including pathogenic organics. Ozone was again widely used because of the generation of chlorinated halogenated purified products (especially trihalomethane, THMS) by chlorine. However, due to the low solubility of ozone in water, ozone gas injected into the liquid decomposes before reacting with pollutants in water, reducing the efficiency of the reaction [8], [9]. In order to overcome this disadvantage of ozone gas, the gas dissolution effect is good and ozone microbubble treatment using improved oxidation process by hydroxyl radicals generated during bubble cracking has been widely carried out in recent years. Water treatment using ozone microbubbles resulted in an 8-34% higher treatment rate than that with pure ozone gas [10]. Ammonia, the main factor of water pollution, was treated with ozone microbubbles, which were very effective for the oxidation of ammonia [11]. Analysis of the effectiveness of dimethylnaphthalene (DEP) in water by treatment with ozone microbubbles in various reaction conditions showed that the mass transfer efficiency of ozone increased with increasing pH [12]. The effect of pH on ozone microbubble treatment was also studied by other researchers, who concluded in agreement that the higher the pH, the better the microbubble treatment effect [13]-[15].

Starting from the need for treatment of mineral water, it is reasonable to use ozone gas (redox potential 2.07 V) for oxidation of Fe^{2+}, one of the unstable components. Among the inorganic materials in mineral water sources, Fe^{2+} that do not undergo sufficient oxidation can be oxidized to Fe^{3+} during storage of mineral water and become precipitates, which do not change the total iron content in mineral water, but may change the physical properties such as turbidity. Therefore, the deposition of mineral water by fully oxidizing Fe^{2+} before bottling can increase the shelf life of mineral water. This is not contrary to the rule (legislation) that the unstable components of mineral water, such as iron, manganese, sulfur, and arsenic, can be removed [2]. The results show that the ozone microbubble technique can be used to clean the Fe^{2+} present in mineral water, and that the pH of mineral water is problematic.

Most mineral water, especially mineral water with CO_2 above 400 mg/L, has a pH below 7, which can also have a negative effect on ozone treatment of mineral water [5]. In addition, CO_2 gas, which is highly soluble in mineral water, makes it difficult for other gases to dissolve in mineral water. Because according to Henry's law of solubility the amount of gas dissolved in water depends on the partial pressure of the gas dissolved in the water, because in mineral water, CO_2 gas is already highly dissolved. Therefore, the effective oxidation and

Un Hwa Choe* and Yong Jun Kim are with Department of Applied Physics, Kim Chaek University of Technology, North Korea (*corresponding author, e-mail: cuh80624@star-co.net.kp).

Jong Hyon Choe is with Department of Food Engineering, Pyongyang Han Tok Su University of Light Industry, North Korea.

deposition of Fe^{2+} by using ozone gas in CO_2-rich mineral water requires a new method of ozone injection and injection conditions to suit the characteristics of mineral water.

The aim of the present study was to use ozone microbubbles to fully oxidize Fe^{2+} to reduce the reference value of drinking water, thus eliminating the occurrence of sediment during storage and increasing the shelf life by 360 days.

In this paper, the effect of the concentration of CO_2 gas in mineral water and the pH of mineral water on the deposition rate of Fe^{2+}, the injection stage of ozone gas was determined, and the change of other ions in mineral water during ozone microbubble treatment was considered.

II. Materials and Methods

A. Preparation of Mineral Water Samples

The mineral water samples used in the experiment were CO_2 -separated from original mineral water containing natural CO_2. The amount of CO_2 in original mineral water is about 3990 mg/L at 15 °C, 0.1 MPa, and the pH of the mineral water is 5.71. The mineral waters are of HCO_3-Ca-Mg-Na type. The amount of CO_2 in mineral water was changed to five values such as 3990 mg/L, 2230 mg/L, 1675 mg/L, 1118 mg/L, and 558 mg/L respectively.

B. Natural Oxidation

The CO_2-separated mineral water was oxidized and precipitated in an air-contacting oxidation column (80 m^3) for 3 days (Fig. 1), and the mineral water sample was sprayed in a jet nozzle mounted at the top of the oxidation column and contacted with air. The mineral water sprayed from the jet nozzle passes through the sand filter bed and is transported to the settling tank through valve 5.

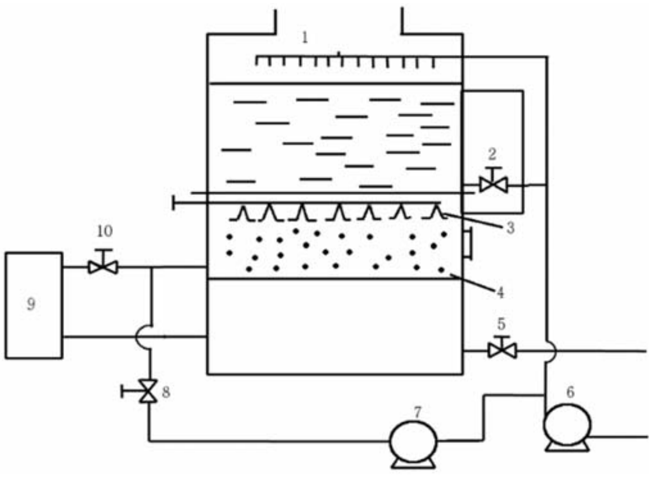

Fig. 1 Structure of the oxidation column: 1-injection nozzles, 2, 5, 8, 10-valves, 3-mixers, 4-sand layer, 6, 7-pumps, 9-level monitor

C. Pure Ozone Gas Oxidization

The experimental diagram is shown in Fig. 2. The air inhaled to the ozone generator is purely oxygen through filtration, compression, water separation and nitrogen separation steps. The passing pressure of oxygen gas in the plate is at a maximum of 0.6 atm and the amount of ozone gas produced in the ozone generator is 6-60 g/h. The experiments were carried out by varying the concentration of ozone gas generated from 0.5 g/h to 5 g/h.

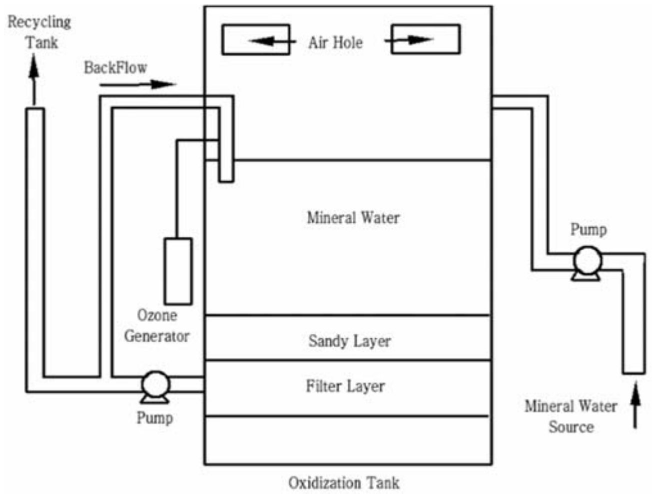

Fig. 2 Schematic of pure ozone gas treatment

D. Ozone Micro bubbles Oxidization

The experiment schematic is shown in Fig. 3. The micro bubble generator (MF5, Shanghai Xingheng Technology, Inc., China) was placed at 0.5 m from the upper liquid side of the reaction tank (80 m^3) and the ozone micro bubbles generated in the generator were passed through the reaction tank. The pressure of mineral water injected into the micro bubble generator is 7 atm, and ozone gas is spontaneously inhaled by the negative pressure generated inside the generator. Ozone micro bubble treated mineral water is discharged to valve 5 through the sand filter bed and transported to the settling tank.

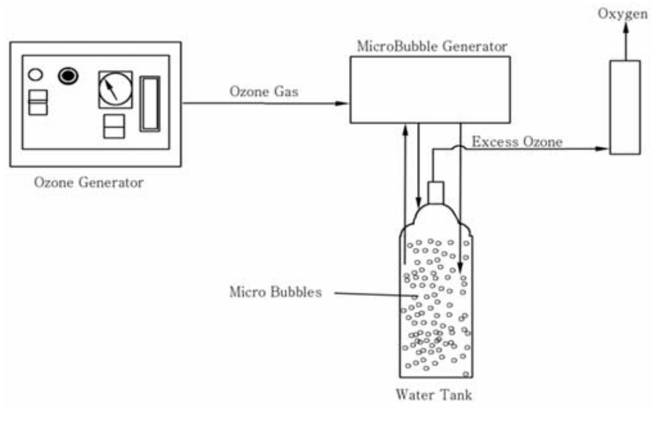

Fig. 3 Schematic of ozone micro bubbles treatment

E. Analysis Methods

The concentration of gaseous ozone was measured by the iodine method [16]. The concentration of ozone dissolved in mineral water was measured by the indigo colorimetric method [16]. The type and amount of cations in the mineral water were analyzed using an atomic absorption spectrometer (Perkin Elmer 5100 PC, USA). And, the type and amount of anions were analyzed using the acid titration method. The settling time was determined as the time taken from the start of oxidation to the acceptable turbidity by extracting mineral water from the oxidation tank at a certain time interval and measuring its turbidity. The turbidity was measured using HACH 2100P (Hach Company, Loveland, USA).

III. Results and Discussions

A. Effectiveness of Oxidation by Ozone Microbubbles

For mineral water with a CO_2 gas content of 558 mg/L, the changes in turbidity with time were observed for natural oxidation, pure ozone gas oxidation and ozone microbubble oxidation (Fig. 4). Fig. 4 shows that the turbidity of natural oxidized mineral water gradually decreases with time and is 70 h of settling time until it becomes an acceptable turbidity according to drinking water standards.

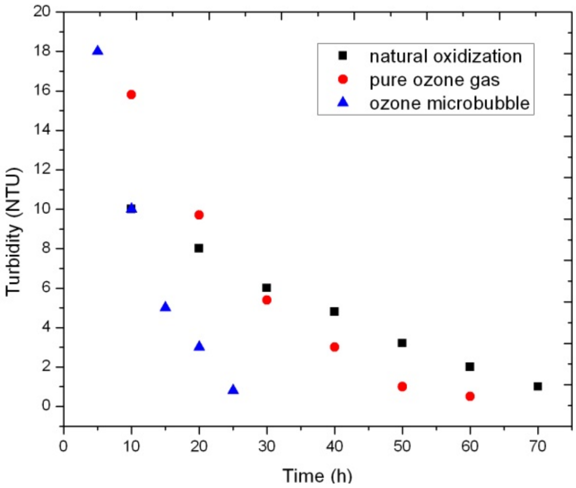

Fig. 4 Turbidity change with time for different oxidization methods

In the case of pure ozone gas oxidation, the reference turbidity was satisfied for 50 h. The settling time for oxidation by ozone microbubbles is about 25 h. The effect of oxidation by ozone gas is better compared to natural oxidation, especially the effect of ozone microbubble oxidation is three times higher. The amount of residual ozone in the solution in the oxidation by ozone gas is 1 mg/L, and the amount of residual ozone in the oxidation by ozone microbubbles is 25.6 mg/L, which is about 52 times higher than the solubility of ozone gas at room temperature. This means that the concentration of dissolved ozone in oxidation by ozone microbubbles is higher and the ozone availability is higher compared to oxidation by ozone gas.

The internal pressure of the bubble, which has a large influence on the solubility, depends strongly on the size of the bubble. The Young-Laplace equation [17] can be used to calculate the internal pressure of bubbles.

$$Pg = p_1 + \frac{4\sigma}{d_b} \quad (1)$$

where, p_g is the gas pressure (Pa) inside the bubble and p_1 is the pressure (Pa) of the bubble outer liquid; σ is the surface tension of bubbles (N m^{-1}), and d_b is the diameter of the bubble (m). According to (1), the internal pressure of 1 μm bubble is 3.85 times larger compared to the internal pressure of 1 mm bubble. Therefore, micro-bubbling of ozone gas increases the partial pressure of ozone gas due to the increase in pressure due to the decrease in surface area, which increases the solubility of ozone gas. Oxidation by ozone microbubbles generates more hydroxyl radicals because of the large mass transfer coefficient of ozone gas due to the increased contact cross-section of ozone gas and water. In addition, hydroxyl radicals are generated during the cracking of microbubbles, the redox potential of hydroxyl radicals is 0.73 eV higher than that of ozone gas, which also plays a role in enhancing the additional oxidation capacity of ozone gas [15]. Therefore, it can be seen that the oxidation process by ozone microbubbles increases the dissolution concentration of ozone and improves the production of hydroxyl radicals.

B. Effect of CO_2 Concentration on Ozone Microbubble Treatment

Fig. 5 shows the turbidity variation measured at five-hour intervals from the start of ozone microbubble treatment in mineral water with different CO_2 gas concentrations. At this time, the size of ozone microbubbles is about 80 μm. When the CO_2 gas content is 1118 mg/L, the deposition time is about 25 h, about 35 h for 1675 mg/L and about 40 h for 2230 mg/L. It can be seen that the deposition time increases gradually with increasing CO_2 gas content.

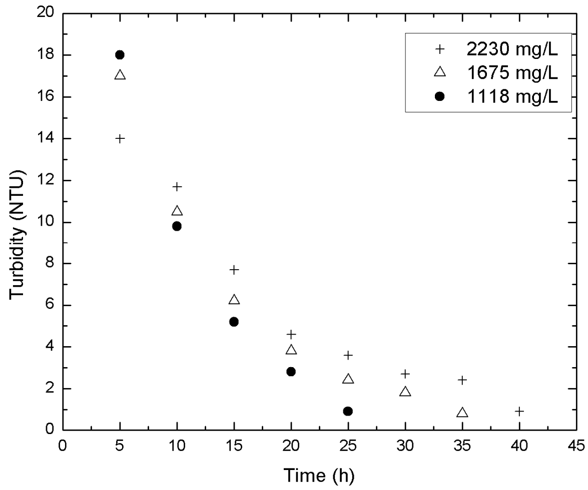

Fig. 5 Turbidity change with time in different concentration of CO_2 for ozone microbubbles treatment

As can be seen from Fig. 5, the CO_2 content in the mineral water certainly affects the ozone gas bubble treatment. The fact that the deposition time decreases with decreasing CO_2 content means that ozone gas is dissolved in water much, thereby accelerating the oxidation of Fe^{2+}. In fact, according to Henry's solubility law, the mole fraction for water at 20 °C and 0.1 MPa is 7.07×10^{-4} for CO_2, whereas 1.885×10^{-6} for O_3, CO_2 is about 375 times larger than O_3. Therefore, it is difficult to dissolve ozone gas more in mineral water sources with high CO_2 solubility. On the other hand, the values of the distribution coefficient H for the solubility of different gases in water are shown in Table I [18].

TABLE I
DISTRIBUTION COEFFICIENT H FOR THE SOLUBILITY IN WATER [18]

Compound	Distribution coefficient H		
	0 °C	10 °C	20 °C
Nitrogen, N_2	0.023	0.019	0.016
Oxygen, O_2	0.049	0.041	0.033
Methane, CH_4	0.055	0.043	0.034
Carbon dioxide, CO_2	1.71	1.23	0.942
Hydrogen sulfide, H_2S	4.69	3.65	2.87
Ozone, O_3	0.64	0.54	0.39

As shown in Table I, the distribution coefficient H for CO_2 is about 2.4 times larger than that for O_3.

Gases with low values of the distribution coefficient H are difficult to dissolve in water, and gases with high values of the distribution coefficient H are prone to dissolve in water. Therefore, 3990 mg/L of CO_2 gas in mineral water source would prevent additional dissolution of O_3. With the removal of CO_2 gas from mineral water source, the amount of dissolved in water increases, resulting in a decrease in deposition time. According to experiments, it is clear that the ozone microbubble injection step should be chosen as sufficiently CO_2-removed step from the mineral water.

C. Effect of pH on Ozone Micro Bubble Treatment

In the case of ozone microbubble treatment, the variation of residual ozone concentration and pH with the change of CO_2 gas concentration in mineral water is given in Table II.

TABLE II
RESIDUAL OZONE CONCENTRATIONS AND PH VALUES DEPENDING CO_2 CONCENTRATION IN MINERAL WATERS

No.	CO_2 Concentration, mg/L	Residual ozone concentration, mg/L	pH
1	3990	-	5.8
2	2230	4	6.2
3	1675	8	6.4
4	1118	12	6.5
5	558	25.6	6.9

As shown in Table II, as the content of CO_2 in mineral water decreases, the pH increases and the residual ozone concentration increases. When the CO_2 content in original mineral water was 3990 mg/L, the pH was 5.8 and the residual ozone concentration was not observed, whereas the pH was 6.9 and the residual ozone concentration was 25.6 mg/L, when the CO_2 content in mineral water was 558 mg/L. This indicates that the decrease in CO_2 content of mineral water increases the solubility of ozone microbubbles, and at the same time increases the pH value of mineral water, which makes the water treatment effect by ozone microbubbles favorable. According to [7], the decomposition reaction of ozone in water varies in character depending on the pH value. Under acidic conditions of solution (Ph < 7), direct oxidation reactions with molecular ozone and microorganisms dominate, and at pH~7, indirect reactions with radicals that occur when ozone is dissolved in water and direct reactions occur simultaneously. In the case of pH > 7, organic compounds do not react with molecular ozone, and continuous decomposition of ozone occurs with increasing pH value. In Fig. 4, the good effect of ozone microbubble treatment with a of 558 mg/L in mineral water is seen as an increase in the solubility of ozone microbubbles with a decrease in CO_2 content, while the pH of mineral water is 6.9 (Table II), which indicates that the generation of hydroxyl radicals with direct reaction of ozone molecules occurs explosively and the oxidation effect by ozone is improved.

From the above experimental results and discussions, it can be seen that the ozone injection step, which is reasonable for the effect of water treatment by ozone microbubbles in mineral water with high CO_2 content, is a step in which the content of CO_2 is controlled so that the pH value of mineral water is about 7 or above 7. In the mineral water used in this paper, its value is 558 mg/L.

D. Effect of Ozone Microbubble Treatment on Ion Concentration in Mineral Water

The main components of the ozone microbubble treated mineral water with 558 mg/L CO_2 concentration are analyzed in Table III.

TABLE III
RESULTS OF THE ANALYSIS OF IMPORTANT COMPONENTS OF OZONE MICROBUBBLE TREATED MINERAL WATER (MG/L)

Component object	Fe	Na	K	Ca	HCO_3^-	Cl^-
Before	0.14	45.3	12.2	117.4	707.6	63.03
After	0.01 >=	46.3	11.9	56.7	695.4	62.6

As shown in Table III, the concentrations of K^+ and Na^+ were almost unchanged before and after the ozone microbubble treatment, and the concentration of Ca^{2+} decreased by half. This indicates that the oxidation process of mineral water by ozone microbubbles does not change the amount of ions that are beneficial to the human body.

IV. CONCLUSION

Ozone microbubbles can be used to improve the oxidation of CO_2–rich mineral water. The injection of ozone microbubbles into mineral water with CO_2 of 3390 mg/L did not show a good treatment effect. It is due to the effect of pH on ozone treatment and CO_2 dissolved in mineral water.

The separation of CO_2 from mineral water and injection of ozone microbubbles enhances the solubility of ozone gas in mineral water. For a residual CO_2 of 558 mg/L, ozone microbubble treatment reduced the deposition time by 1/3 compared to natural oxidation, and the concentration of iron ions decreased from 0.14 mg/L before treatment to 0.01 mg/L after treatment. At this time, the shelf life increased from 30 days to 360 days. This is because the solubility of microbubbles is high and oxidation due to the generation of hydroxyl radicals is improved. Ozone microbubble treatment method for mineral water with high CO_2 content can be used for wastewater treatment with high harmful gas content.

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