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Removal of iron and manganese ions from abandoned neutral or alkaline mine drainage via ozone oxidation and micro-sand filtration: a pilot-scale operation

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ABSTRACT

The objective of this study was to evaluate the ozone oxidation of dissolved Fe and Mn ions in abandoned neutral or alkaline mine drainage (NAMD) and the subsequent micro-sand filtration by conducting a pilot-scale operation with several ozone doses in an ozone reactor. The effects of the hydraulic retention time on the ozone oxidation were also investigated. The pH values were either neutral or slightly alkaline and the average Fe and Mn concentrations in the abandoned NAMD were 25.5 and 2.06 mg/L, respectively. The experiment results indicated that six-hour ozone oxidation with an ozone dose of 24.0 g O_3/h (i.e. initial ozone concentration: 3.53 mg O_3/L) and subsequent micro-sand filtration could meet the drinking water quality standard (less than 0.3 mg/L) for both Fe and Mn in the micro-sand filter effluent. The hydraulic retention time of the ozone reactor at this ozone dose was 106 s, and the media of sand grains were between 0.4 and 0.7 mm in diameter. The total dissolved solids, alkalinity, and SO_4^{2-} concentrations of the influents were virtually unchanged in this pilot-scale operation. However, the oxidation-reduction potential of about 18 mV in influents increased rather gradually in effluents, and was recorded in the range of 185–210 mV during ozone oxidation. The ozone oxidation and subsequent micro-sand filtration under the operating conditions, in this study, appear to be among the desirable alternatives for the effective removal of dissolved Fe and Mn in the form of metal precipitates during ozone oxidation. This alternative could prevent metal precipitates from settling at the bottom of local water channels by removing them before they are discharged into streams.

Keywords: Abandoned neutral or alkaline mine drainage (NAMD); Dissolved heavy metals; Micro-sand filtration; Ozone oxidation; Pilot-scale operation

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1. Introduction

Abandoned mine drainage is an important source of metal contamination in the vicinities surrounding 261 of the approximately 1,230 officially abandoned or closed mines throughout Korea [1,2]. In general, abandoned mine drainage appears to be extremely acidic and has been called acidic mine drainage (AMD). It is rich in iron, aluminum, sulfate, and heavy metals such

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as mercury, cadmium, and manganese [3]. In contrast to the AMD, neutral or alkaline mine drainage (NAMD) has alkalinity that exceeds acidity, but also has elevated concentrations of SO_4^{2-}, Fe^{2+}, Mn^{2+}, and other solutes [4]. Reddish–brown precipitates associated with abandoned NAMD are frequently observed at the bottom of small local stream channels in Kangwon and Chungbuk provinces, Korea. Colored precipitates are known to be produced by chemical processes such as the neutralization of acidic inputs, oxidation, and precipitation of metal oxyhydroxides. Precipitates can scavenge other metals in the water column and can either be transported downstream or can aggregate and settle on the bed sediment [5,6]. The chemical composition of some precipitates in the abandoned NAMD near the Donghae coal mine in Korea was analyzed via energy-dispersive X-ray fluorescence (XRF) during a one-year monitoring survey [7]. Fe_2O_3 and SO_3 were the major constituents of the brownish–yellow precipitates, accounting for 58.53 and 13.73%, respectively. Al_2O_3 and SO_3 were the principal constituents of the white precipitates, accounting for 43.34 and 16.75%, respectively.

The chemistry of conventional and alternative treatment systems for the neutralization of abandoned NAMD has been critically reviewed [8]. The lime neutralization process is the most commonly used treatment worldwide. The chemical oxidation of dissolved heavy metals with air, oxygen, hydrogen peroxide, calcium peroxide, ozone, chlorine, potassium permanganate, and chlorine dioxide was also evaluated as to its possible treatment of acidic mineral process discharges and groundwater [9,10]. It is known that iron (II) and manganese (II), which are present in natural water, can be quickly oxidized by ozone into insoluble oxides and hydroxides. One of the major mechanisms is electron transfer from the reduced metal to ozone, which forms Fe(III), the reduced radical O_3^-, and the OH radical [11]. In the presence of an excessive amount of Fe(II), the OH radical can oxidize a second Fe(II). The other mechanism involves oxygen transfer from ozone to Fe(II). A critical review of the ozonation of drinking water suggests the two major oxidants, ozone and OH radicals, govern the chemical processes during the ozonation of water [12]. The oxidation of inorganic micro-pollutants (e.g. Fe(II), Mn(II), H_2S, and NO_2^-) by ozone is known to be generally fast and very efficient. The most prominent exception is ammonia, which is only slowly oxidized by ozone and OH radicals. Research has been conducted on the ozone oxidation of heavy metals, but has been unable to provide practical ranges for the operating conditions, such as the ozone dose and the hydraulic retention time (i.e. the contact time for the oxidation) in a pilot-scale ozone reaction. The objective of this study was to evaluate the ozone oxidation of dissolved Fe and Mn ions in abandoned NAMD and subsequent micro-sand filtration by conducting a pilot-scale operation using several ozone doses in an ozone reactor. The effects of the hydraulic retention time on the ozone oxidation were also investigated using three different retention times of the ozone dose.

2. Materials and methods

A pilot-scale turbulent jet-flow contactor (TJC) system was installed with a nominal flow capacity of $6.8\,m^3/h$. This system consists of influent pumps (PU-350 M and PU-954 M, WILO), an oxygen generator (AS-B(45), AIRSEP), an ozone generator (CFS-1 2G, OZONIA), an ozone injector, a 200 L stainless steel ozone reactor, an air vent (11 AV, Armstrong), an ozone destructor, a sand filter column, and a granular activated carbon (GAC) column. The components of the pilot-scale plant were interconnected with stainless steel pipes. A portion of the abandoned NAMD near the Jungam Mine in Samchuck, Korea was pumped into this pilot-scale TJC system and used as an influent for the ozone oxidation. A schematic of the pilot-scale plant is shown in Fig. 1 [2].

The effects of the ozone reactor's hydraulic retention times on the ozone reaction were determined with the three different retention times of 106, 114, and 124 s at an ozone dose of $24.0\,g\,O_3/h$. The ozone oxidation was also initiated with five different ozone doses of 7.5, 12.0, 24.0, 36.0, and $48.0\,g\,O_3/h$ at the hydraulic retention time of 106 s. It is noted that the doses of 7.5, 12.0, 24.0, 36.0, and $48.0\,g\,O_3/h$ represented the initial ozone concentrations of 1.10, 1.77, 3.53, 5.30, and $7.07\,mg\,O_3/L$, respectively, at the hydraulic retention time of 106 s. All experiments were performed in the continuous mode. Neither the temperature nor the pH level of the system was controlled. During the six-hour continuous operation, the effluent of the ozone reactor was pumped into the micro-sand filter column at a surface overflow rate of $5.03\,m^3/m^2\,h$. The media of sand grains were between 0.4 and 0.7 mm in diameter. A portion of the filtered water was kept in a treated water storage tank for future use as backwashing water, and the rest of the filtered water was discharged into the nearby stream. The granular GAC column was installed for safety to remove some organic compounds that had been dissolved, but it was never used because organic compounds were not detected in the NAMD. After the six-hour operation, the filtration phase was terminated and the micro-sand filter was backwashed to remove

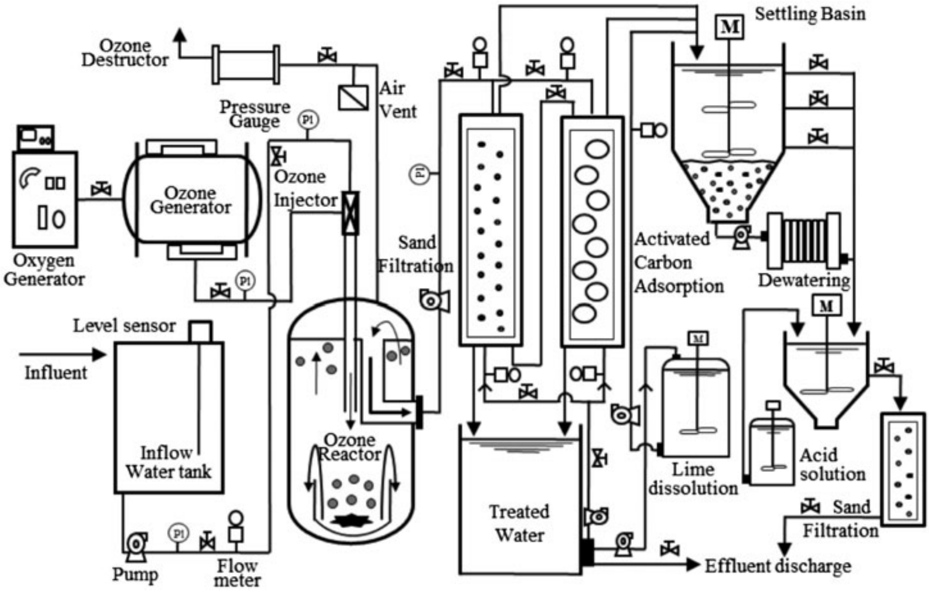

Fig. 1. Schematic of the pilot-scale plant for the removal of iron and manganese ions from abandoned NAMD via ozone oxidation and micro-sand filtration.

the metal oxide and hydroxide precipitates within the micro-sand filter bed. The backwashing was conducted for about 10 min by reversing the flow from the water storage tank to the filter. The washwater that contained the precipitates was returned to a settling basin to which lime was added to thicken the precipitates. The thickened precipitates were finally dewatered and removed as a reddish–brown cake by the plate filter press (ID50-30, Dewatering Inc., Korea).

Samples from the micro-sand filter column were regularly collected during the six-hour continuous operation (before the start of the backwashing) and analyzed for the presence of EC using an HI-98129 tester (USA) and for oxidation-reduction potential (ORP) using an ORP-200 meter (USA). The pH, SO_4^{2-}, color, alkalinity, and total dissolved solids (TDS) were also analyzed according to the standard methods [13]. The concentrations of Fe, Mn, Al, Cr, and Hg were measured using ICP-AES (Japan) with a Thermo IRIS Intrepid II spectrometer (UK). The standard 3120B digestion method was used for metals analysis.

3. Results and discussion

3.1. Typical characteristics of abandoned NAMD

A series of experiments were performed for the ozone oxidation of the dissolved metals in the abandoned NAMD. The typical characteristics of the abandoned NAMD near the Jungam Mine are shown in Table 1.

Table 1
Typical characteristics of the abandoned NAMD from the Jungam Mine in Samchuck, Korea

Constituents	Average concentration	Range
pH	7.18 (median)	7.10–7.28
TDS (mg/L)	381	318–398
EC (μs/cm)	762	697–799
ORP (mV)	29	16–48
SO_4^{2-} (mg/L)	368	320–379
Fe (mg/L)	25.47	25.0–25.9
Mn (mg/L)	2.06	2.02–2.13
Al (mg/L)	Not detected	
Cr (mg/L)	Not detected	
Hg (mg/L)	Not detected	
Alkalinity (mg/L as $CaCO_3$)	121	110–145
Color (units)	407	235–497

In a preliminary investigation, the total Fe and Mn concentrations (i.e. the sums of the soluble and particulate concentration of the metals in solutions) in an influent of the abandoned NAMD were 11.5 and 4.13 mg/L, respectively. The soluble Fe and Mn concentrations were 8.65 and 2.70 mg/L, respectively, which accounted for 75.5 and 65.4% of the total concentrations of Fe and Mn, respectively. The preliminary investigation also revealed the soluble Fe and Mn concentrations in the effluent of the micro-sand filtration (hydraulic retention time of the reactor: 106 s;

ozone dose: 24.0 g O_3/h) were 0.78 and 0.5 mg/L, respectively, which accounted for 90.9 and 81.5% of the total Fe and Mn concentrations, respectively. These results indicated most of the soluble iron and manganese in the abandoned NAMD were oxidized via ozone and removed in the form of metal particulates during the micro-sand filtration. The total concentrations of Fe and Mn in solutions, hereafter in this study, were only monitored.

The Fe concentrations of the abandoned NAMD ranged from 25.0 to 25.9 mg/L, with an average concentration of 25.5 mg/L. The Mn concentrations of the abandoned NAMD ranged from 2.02 to 2.13 mg/L, with an average concentration of 2.06 mg/L; other heavy metals, such as Al, Cr, and Hg, were not detected. The pH levels ranged from 7.10 to 7.28, with a median value of 7.18. It is noted that the abandoned NAMD was either neutral or slightly alkaline for the duration of this study. The average SO_4^{2-} concentration was relatively high at 368 mg/L, within 350–379 mg/L. The average concentrations and ranges of these observed concentrations with respect to TDS, EC, ORP, alkalinity, and color are also shown in Table 1.

As mentioned above, NAMD has usually alkalinity that exceeds acidity, but also has relatively high concentrations of SO_4^{2-}, Fe^{2+}, Mn^{2+}, and other solutes. One of the typical coal mine drainages was reported near the C & K in Clarion County, Pennsylvania [4]. The pHs in this mine drainage ranged from 6.7 to 7.0. The Fe concentrations ranged from 0.04 to 5.70 mg/L and Mn concentrations ranged from 5.10 to 19.00 mg/L, respectively. The alkalinities were reported to be between 260 and 750 mg/L as $CaCO_3$, and SO_4^{2-} concentrations were between 1,300 and 2,300 mg/L in the mine drainage. Another coal mine drainage was found around the Kauffman Mine in Clearfield County in Pennsylvania, the pHs in this mine drainage ranged from 7.1 to 7.3 [4]. The Fe concentrations were reported to be ranged from 0.12 to 1.10 mg/L and Mn concentrations ranged from 0.15 to 0.26 mg/L, respectively. The alkalinities were reported to be between 126 and 134 mg/L as $CaCO_3$, and SO_4^{2-} concentrations were between 13 and 18 mg/L in the mine drainage. It is noted that NAMD rather appeared to be found in coal mine areas in USA or near Jungam Mine, in Samchuck, Korea, as shown in Table 1.

3.2. The effect of retention times on abandoned NAMD

The experimental results at the doses of 7.5 and 24.0 g O_3/h were discussed in detail in a previous study [2]. The retention time of the ozone reactor was 106 s. The paper showed the concentrations of Fe and Mn in the micro-sand filter effluents were low, at 0.03 and 0.10 mg/L, respectively, during the six-hour continuous operation with an ozone dose of 24.0 g O_3/h. The subsequent micro-sand filtration could therefore meet the Korean drinking water quality standard (less than 0.3 mg/L) for both Fe and Mn in the micro-sand filter effluent with that retention time of 106 s.

The effects of the hydraulic retention times of the ozone reactor on the ozone reaction were further investigated with the three different retention times of 106, 114, and 124 s at the ozone dose of 24.0 g O_3/h. It is also noted that the initial ozone concentrations were 3.53, 3.80, and 4.13 mg O_3/L with those retention times of 106, 114, and 124 s, respectively, at the ozone dose of 24.0 g O_3/h. The major constituents of the effluents of the micro-sand filter column during the first six-hour continuous operation are shown in Fig. 2. The initial concentrations of such major constituents in the influents (given in the figure title) were intentionally not included in Fig. 2, which shows only a simple comparison of the concentration variation during the entire course of the six-hour ozone oxidation and the subsequent micro-sand filtration. The longer the retention times were, the higher the Fe and Mn concentrations of the sand filter effluents, as shown in Fig. 2(a). The gradual increases in the Fe and Mn concentrations of the effluents were also observed with respect to the reaction times that elapsed in the reactor. The reason for these increases in the Fe and Mn concentrations of the effluents when the retention times of the reactor increased from 106 to 124 s was not clear. However, these increases at an ozone dose of 24.0 g O_3/h might be because the sand filter was overloaded with the large amount of metal oxide and hydroxide precipitates that formed when the reactor retention times increased in this study. In particular, the Fe concentrations of the effluents were less than 0.3 mg/L for the first three hours of the operation with the hydraulic retention time of 124 s, after which the Fe concentrations increased rapidly to 0.468, 0.924, and 1.387 mg/L at the reaction times of four, five, and six hours, respectively. The Mn concentrations in the micro-sand filter effluents were observed to have been higher than 0.3 mg/L after the first 30 min of the operation with the same hydraulic retention time (Fig. 2(a)). The effects of shorter retention times of less than 106 s on ozone oxidation should be further evaluated.

The pH levels in the influents ranged from 7.14 to 7.28. The pH levels of the effluents gradually increased with the retention time of 124 s and reached a steady pH of 7.22 at the reaction time of three hours. No remarkable variation of the pH levels was observed with the retention times of 106 and 114 s with respect to the reaction time, as shown in Fig. 2(b). The ORP of 50 mV in the influent increased rapidly to 202 mV in

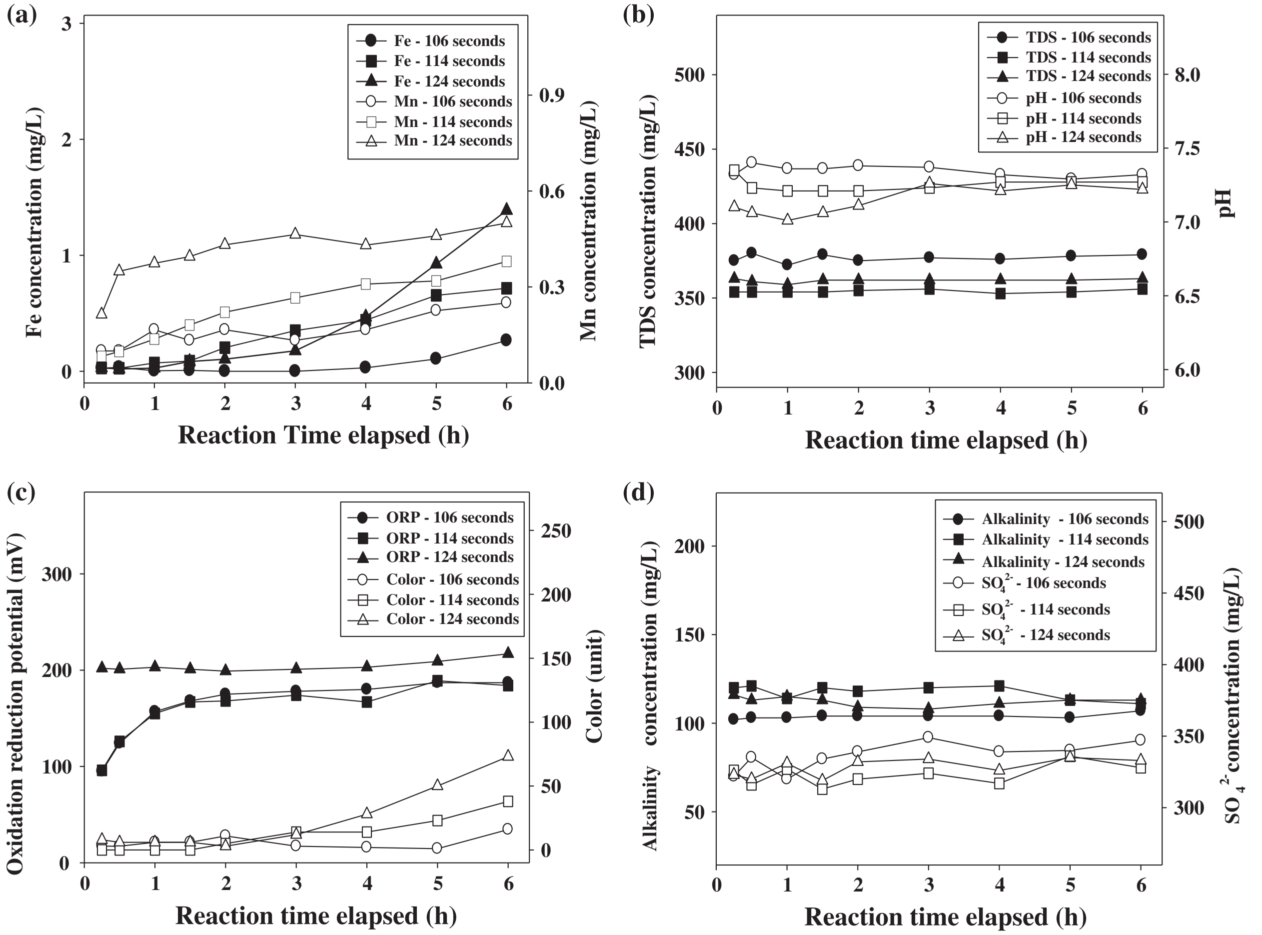

Fig. 2. Major constituents of the effluents of the micro-sand filter column during the first six-hour continuous operation with the three hydraulic retention times of 106, 114, and 124 s at the ozone dose of 24.0 g O_3/h. (a) The concentration profiles of Fe and Mn, (b) the concentration profiles of TDS and their pH levels, (c) the ORPs in terms of the mV and color in the standard units, and (d) their alkalinity in mg/L as $CaCO_3$ concentrations and the concentration profiles of SO_4^{2-} with respect to the elapsed times. The average Fe and Mn concentrations in the influents were 25.56 and 2.09 mg/L, respectively. The influent concentration ranges of Fe and Mn were 25.40–25.71 mg/L and 2.03–2.13 mg/L, respectively. The initial concentrations of such major constituents in the influents were intentionally not included in Fig. 3, as shown in Fig. 2. It is noted that the average influent concentrations of TDS, pH, ORP, color, alkalinity, and SO_4^{2-} ions were 351 mg/L, 7.23, 29 mV, 353 units, 118 mg/L, and 346 mg/L, respectively. The influent concentration ranges of TDS, pH, ORP, color, alkalinity, and SO_4^{2-} ions were 318–389 mg/L, 7.14–2.28, 18–48 mV, 235–497 units, 110–129 mg/L, and 320–367 mg/L, respectively.

the effluent of the sand filtration after 15 min of oxidation with the retention time of 124 s, as shown in Fig. 2(c). The ORPs of the effluents were then steadily maintained at about 210 mV for the rest of the oxidation period. However, the ORP of 18 mV in the influent increased gradually to about 95 V in the effluent of the sand filtration after 15 min of oxidation with retention times of 106 and 114 s. The ORP of the effluents reached about 170 mV for the first two hours of the operation, after which it increased slightly and was 185 mV at the reaction time of six hours.

The colors of the influents were 497, 235, and 326 units with the retention times of 106, 114, and 124 s, respectively. The color of the influents decreased rapidly to about four units in the effluent of the micro-sand filtration after 15 min of oxidation in the ozone reactor, as shown in Fig. 2(c). The color of the effluents remained less than six units for the first five hours of the operation with the retention time of 106 s, after which the color increased slightly and was 16 units at the reaction time of six hours. However, the color of the effluents gradually increased with the retention times of 114 and 124 s and was 38 and 78 units, respectively, at the reaction time of six hours.

The effects of the hydraulic retention times of the ozone reactor on the ozone reaction were generally observed in the last three hours of the entire six-hour pilot-scale operation. For the concentrations of Fe and Mn and the color of the effluents of the micro-sand filter, the retention time of 106 s appeared to be the desirable alternative among the three retention times investigated in this study. The results indicate a new possible continuous operating time of three hours, right before the start of the backwashing, could be considered in the future. The TDS, alkalinity, and SO_4^{2-} concentrations of the influents were virtually unchanged during the six-hour ozone oxidation and the subsequent micro-sand filtration, as shown in Fig. 2(b) and (d).

3.3. The effect of ozone doses on abandoned NAMD

Fig. 3 shows the concentration profiles of Fe and Mn in the effluents of the micro-sand filter during the six-hour continuous operation of the ozone reactor, right before the start of the backwashing, with relatively higher ozone doses of 7.5, 12.0, 24.0, 36.0, and 48.0 g O_3/h added to the reactor. The hydraulic retention time in the ozone reactor was, hereafter, 106 s with these ozone doses throughout this study. It is better mentioned that the doses of 7.5, 12.0, 24.0, 36.0, and 48.0 g O_3/h represented the initial ozone concentrations of 1.10, 1.77, 3.53, 5.30, and 7.07 mg O_3/L, respectively, at the hydraulic retention time of 106 s. The influent concentration ranges (i.e. the concentrations at the initiation of the first six-hour continuous operation of the ozone reactor) of Fe and Mn were 25.01–25.92 mg/L and 2.03–2.13 mg/L, respectively. Since the difference between the minimum and maximum concentrations in the influent concentration ranges appeared to be relatively small, the influent concentrations of Fe and Mn (given in the figure title) were intentionally not included in Fig. 3.

The ozone oxidation was initiated at an ozone dose of 7.5 g O_3/h with a hydraulic retention time of 106 s. The Fe concentration of 25.06 mg/L in the influent decreased rapidly to 0.012 mg/L of the effluent of the micro-sand filtration after 15 min of oxidation in the ozone reactor, as shown in Fig. 3(a). The Fe concentration of the effluents was less than 0.3 mg/L for six hours of the operation. This indicates that six-hour ozone oxidation with an ozone dose of 7.5 g O_3/h and subsequent micro-sand filtration can meet the Korean drinking water quality standard for Fe in the micro-sand filter effluent. The higher the ozone doses were, the higher the Fe concentrations in the sand filter effluents became, as shown in Fig. 3(a). In particular, the Fe concentrations of the effluents were less than 0.3 mg/L for the first four hours of the operation with an ozone dose of 36.0 g O_3/h, after which the Fe concentrations increased slightly to 0.404 and 0.584 mg/L at the reaction times of five and six hours, respectively. The Fe concentrations of the effluents were less than 0.3 mg/L for the first two hours of the operation with an ozone dose of 48.0 g O_3/h, after which the Fe concentrations increased rapidly to 0.512, 0.956, 1.358, and 1.400 mg/L at the reaction times of three, four, five, and six hours, respectively. Fe concentration increases of the effluents at high ozone doses of 36.0 and 48.0 g O_3/h might have occurred for the same reason that Fe and Mn concentrations in the micro-sand filter effluents increased when retention times

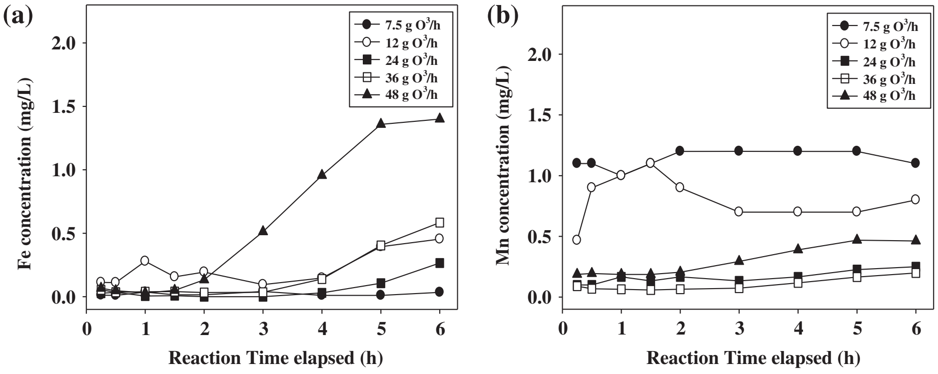

Fig. 3. Profiles of the Fe and Mn concentrations in the effluents of the micro-sand filter during the first six-hour continuous operation of the ozone reactor, right before the start of the backwashing, with ozone doses of 7.5, 12.0, 24.0, 36.0, and 48.0 g O_3/h added to the reactor (reactor volume: 200 L). The hydraulic retention time in the ozone reactor was 106 s with these ozone doses. The average Fe and Mn concentrations in the influents were 25.47 and 2.06 mg/L, respectively. The influent concentration ranges of Fe and Mn were 25.01–25.92 mg/L and 2.03–2.13 mg/L, respectively. It is noted that the influent concentrations of Fe and Mn were intentionally not included in the figures as the difference between the minimum and maximum concentrations in the influent concentration ranges appeared to be relatively small.

increased, namely because the sand filter was overloaded with the large amount of metal oxide and hydroxide precipitates that formed during oxidation.

The Mn concentrations in the micro-sand filter effluents were higher than 0.7 and 1.0 mg/L at low ozone doses of 7.5 and 12.0 g O_3/h, respectively, as shown in Fig. 3(b). This indicated that the six-hour ozone oxidation with theses ozone doses could not meet the Korean drinking water quality standard for Mn (less than 0.3 mg/L). This might be due to that the conversion of Mn^{2+} into MnO_2 requires more oxidizing power or energy than the conversion of Fe^{2+} into $Fe(OH)_3$ [14]. The pilot-plant was subsequently operated at higher ozone doses of 24.0, 36.0, and 48.0 g O_3/h. The Mn concentrations of 2.08 mg/L in the influent decreased rapidly to 0.10 and 0.09 mg/L in the micro-sand filtration effluents after 15 min of oxidation in the ozone reactor with ozone doses of 24.0 and 36.0 g O_3/h, respectively (Fig. 3(b)). The Mn concentrations of the effluents were less than 0.3 mg/L for the first three hours of the operation with an ozone dose of 48.0 g O_3/h, after which the Mn concentrations increased to 0.389, 0.468, and 0.462 mg/L at the reaction times of four, five, and six hours, respectively. When the ozone doses increased from 24.0 to 48.0 g O_3/h, the manganese concentrations increased gradually and consistently in the effluents. It could be interpreted in two possible ways [15]. One was that higher ozone dose oxidized more small manganese particles to clog rapidly the surface of subsequent filter resulting in rapid breakthrough. The other could be that the higher ozone dose over-oxidized manganese ions to form Mn^{+7}, which was soluble form having pink color. The ozone doses for the lowest Fe and Mn concentrations ever achieved in the micro-sand filter effluents during the six-hour continuous operation of the ozone reactor were 7.5 and 36.0 g O_3/h, respectively. These experimental results suggest a six-hour ozone reaction with an ozone dose of 24.0 g O_3/h at the retention time of 106 s and the subsequent micro-sand filtration can meet the Korean water quality standard for both Fe and Mn in the micro-sand filter effluent.

XRF analysis was performed in order to investigate the chemical composition of precipitate formation in the backwashing water. The result of the XRF analysis (Rigaku ZSX100e, Rigaku Industrial Corporation, Japan), which delineated the ratio of metal oxides and hydroxides formed in the backwashing water with the four different ozone doses, is shown in Table 2. In this analysis, Fe_2O_3 appeared to be a major component in the backwashing water and accounted for 71.6, 86.6, 82.7, and 75.3% at the ozone doses of 7.5, 12.0, 24.0, and 36.0 g O_3/h, respectively. MnO_2, which appeared to be the second major component in the backwashing water, accounted for only 8.63, 0.309, 3.78, and 11.1% at the four different ozone doses. This result indicates the percentage content of the major component, Fe_2O_3, in the backwashing water decreased as the ozone dose increased from 12.0 to 36.0 g O_3/h, even if the pattern in the percentage content variation was opposite that for MnO_2.

Table 2
The XRF analysis of the backwashing water at four different ozone doses

	Ozone dose (g O_3/h)			
Component (mass %)	7.5	12.0	24.0	36.0
Na_2O	0.109	0.103	0.0586	0.0732
MgO	0.412	0.415	0.442	0.468
Al_2O_3	1.71	0.653	0.512	0.494
SiO_2	7.62	4.78	4.81	4.13
P_2O_5	0.0335	0.0180	0.0165	0.0128
SO_3	1.61	1.76	1.81	1.79
Cl	0.0179	0.0217	0.0142	0.0165
K_2O	0.208	0.0729	0.0748	0.0705
CaO	6.43	4.76	5.31	5.89
MnO_2	8.63	0.309	3.78	11.1
Fe_2O_3	71.6	86.6	82.7	75.3
NiO	0.0216	0.0126	0.0136	0.0157
ZnO	0.380	0.256	0.235	0.232
SrO	0.281	0.184	0.215	0.279

As previously mentioned, the thickened metal oxide and hydroxide precipitates from the settling basin were finally dewatered with a fixed-volume, recessed-plate filter press. They were then removed as a reddish–brown cake from the pilot-scale plant. The characteristics of the reddish–brown cake, the concentration profiles of Fe and Mn, and the color of the supernatants from the filter press are shown in Table 3. The amount of the cake produced in wet weight and the water content of the cake varied according to the ozone doses in the reactor. The effects of the ozone doses and retention time on the production of the cake were not clearly observed. The average wet weight of the cake after the four six-hour operations was 61.08 kg, with an average water content of 77.8%. The average concentration of Fe in the supernatants from the filter press was 0.64 mg/L, with a range of 0.202–1.033 mg/L. The average concentration of Mn in the supernatants from the same filter press was 0.200 mg/L, with a range of 0.086–0.400 mg/L. It is recommended that the supernatants from the filter press, which normally contained certain amounts of Fe and Mn or color, be returned to the influent flow stream for further treatment.

Table 3
Characteristics of the reddish–brown cakes, the concentration profiles of Fe and Mn, and the color in the supernatants from the filter press

Ozone dose ($g\ O_3/h$),(retention time inseconds)	Cake production after four six-hour operations (kg in wet weight) and after the first six-hour operation (kg)	Water content (%) of the Cake	Fe (mg/L)	Mn (mg/L)	Color (units)
7.5 (106)	60.43 (15.56)	78.4	0.148	0.400	21
12 (106)	58.10 (17.20)	77.8	1.033	0.126	117
24 (106)	63.14 (16.10)	76.3	0.391	0.126	52
36 (106)	63.90 (17.08)	78.5	0.202	0.086	51
48 (106)	56.57 (10.42)	78.2	0.859	0.191	63
24 (114)	59.97 (15.29)	77.4	0.917	0.226	86
24 (124)	65.47 (16.03)	78.3	0.957	0.237	78
Average	61.08 (15.38)	77.8	0.640	0.200	–

4. Conclusions

A series of pilot-scale operations was conducted, in this study, to provide practical ranges for operating conditions, such as the hydraulic retention times (106, 114, and 124 s) and ozone doses (7.5, 12.0, 24.0, 36.0, and 48.0 $g\,O_3/h$). It is noted that the doses of 7.5, 12.0, 24.0, 36.0, and 48.0 $g\,O_3/h$ represented the initial ozone concentrations of 1.10, 1.77, 3.53, 5.30, and 7.07 $mg\,O_3/L$, respectively, at the hydraulic retention time of 106 s. A portion of the abandoned NAMD near the Jungam Mine in Samchuck, Korea was pumped into a pilot-scale system and used as an influent for ozone oxidation.

The pH levels of the abandoned NAMD were slightly alkaline throughout this study. The Fe concentrations ranged from 25.0 to 25.9 mg/L, with an average concentration of 25.5 mg/L and the Mn concentrations ranged from 2.02 to 2.13 mg/L, with an average concentration of 2.06 mg/L. The experimental results confirmed the results in the previous study, which showed that the six-hour ozone oxidation with an ozone dose of 24.0 $g\,O_3/h$ and subsequent micro-sand filtration could meet the Korean drinking water quality standard (less than 0.3 mg/L) for both Fe and Mn in the micro-sand filter effluent with the retention time of 106 s. The media of sand grains were between 0.4 and 0.7 mm in diameter. When the retention times of the reactor increased from 106 to 124 s, the Fe and Mn concentrations in the effluents increased consistently at an ozone dose of 24.0 $g\,O_3/h$. This might be because the sand filter was overloaded with the large amount of metal oxide and hydroxide precipitates that formed during oxidation. The effects of shorter retention times of less than 106 s on ozone oxidation should be further evaluated.

The six-hour ozone oxidation only with the ozone doses of 7.5 and 24.0 $g\,O_3/h$ and subsequent micro-sand filtration can meet the Korean drinking water quality standard for Fe in the micro-sand filter effluent. The concentration increases of the effluents with higher ozone doses of 36.0 and 48.0 $g\,O_3/h$ might have been also caused by the sand filter being overloaded with a large amount of metal oxide and hydroxide precipitates. The six-hour ozone oxidation with the ozone doses of 7.5 and 12.0 $g\,O_3/h$ could not meet the Korean drinking water quality standard for Mn. However, the six-hour ozone oxidation with the higher ozone doses of 24.0 and 36.0 $g\,O_3/h$ (except 48.0 $g\,O_3/h$) could meet the drinking water quality standard for Mn. When the ozone doses, however, increased from 24.0 to 48.0 $g\,O_3/h$, the manganese concentrations increased gradually and consistently in the effluents. This might be caused by that higher ozone dose oxidized more small manganese particles to clog rapidly the surface of subsequent filter resulting in rapid breakthrough. Otherwise, it could be that higher ozone dose over-oxidized manganese ions to form Mn^{+7}, which was soluble form having pink color.

The six-hour ozone oxidation with an ozone dose of 24.0 $g\,O_3/h$ at a retention time of 106 s and subsequent micro-sand filtration under the operating conditions, in this study, appear to be among the desirable alternatives for the effective removal of dissolved Fe and Mn in the form of metal precipitates during ozone oxidation. This alternative could prevent metal precipitates from settling at the bottom of local water channels by removing them before they are discharged into streams.

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