Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2014.927120

53 (2015) 2378–2387
March

Taylor & Francis
Taylor & Francis Group

A study on evaluation of the pipe wall decay constants of residual chlorine and affecting factors in reclaimed water supply system

H.D. Lee[a], J.H. Park[a,*], S.W. Kang[a], M.S. Kong[b]

[a]*Water Resources and Environment Research Department, Korea Institute of Construction Technology, Goyang, Republic of Korea, Tel. +82 31 910 0297; Fax: +82 31 910 0291; emails: hdlee@kict.re.kr (H.D. Lee), jhpark1224@kict.re.kr (J.H. Park), kangsw93@kict.re.kr (S.W. Kang)*

[b]*Construction Environment Engineering, University of Science and Technology-Korea Institute of Construction Technology, Goyang, Republic of Korea, email: mskong@kict.re.kr*

Received 12 April 2013; Accepted 15 July 2013

ABSTRACT

Wall decay reaction of residual chlorine in reclaimed water was evaluated through experiments using the PVC pipe reactor under the lab test conditions. As a result of evaluating the biofilm formation in the supply pipe of reclaimed water, it was confirmed that there were limitations to prevent reclaimed water supply system from the biofilm formation even though residual chlorine existed in reclaimed water. It was confirmed that biofilm was a dominant factor to increase the wall decay constants. The range of wall decay constants under the lab test conditions was within 0.012–0.20 m/d. It implies that wall decay constants showed great dependence on water temperature, initial chlorine concentration, and pipe diameter. Wall decay constants appeared to increase as water temperature increased. Wall decay constants were higher at lower initial chlorine concentration regardless of water temperature and pipe diameter. Depending on pipe diameter, the increased pipe diameter was led to the decreased wall decay constant.

Keywords: Pipe wall decay constants; Reclaimed water supply system; Residual chlorine; Biofilm

1. Introduction

Water scarcity has emerged as a worldwide problem due to the increased world population, climate change, the decrease of available water resources from the seriously contaminated water environment, increased water demand from urbanization and the concentrated population in urban areas, and imbalance on the distribution of water resource among others. It is well recognized to use reclaimed water as one of solutions to secure water resources [1]. However, risk potential and safety issue for human health and ecology by exposure or contact of pathogenic micro-organisms, aesthetic rejection, and deterioration of water quality caused by re-growth of micro-organisms are limiting the use of reclaimed water. For such reasons, it is necessary to introduce the disinfection process such as chlorine disinfection.

While reclaimed water is moving through supply systems after chlorination, residual chlorine concentration is decreasing through reactions between chlorine and bulk water or chlorine and pipe wall.

---

*Corresponding author.

Accordingly, it is necessary to maintain a proper concentration of residual chlorine in the supply system to secure the safety of reclaimed water through preventing the inside of supply system from water quality deterioration and re-growth of micro-organisms. For such a purpose, it is necessary to evaluate residual chlorine decay reactions in the reclaimed water supply system. In other words, it is important in water quality management of the supply system to understand how much chlorine concentration decreases over time by the reaction between residual chlorine and pipe material, accumulated material in the pipe, and several compounds in bulk water [2]. The understanding on residual chlorine decay reaction in the reclaimed water supply system is helpful in establishing the operating strategies for reclaimed water supplier, which can be said to be essential in securing the safety of reclaimed water quality.

Until lately, the studies that are related to prediction of residual chlorine decay in drinking water distribution system have been conducted consistently. However, the study that is intended to evaluate the residual chlorine decay reaction in reclaimed water supply system is still insufficient. In addition, in the case of reclaimed water supply system, few studies have been conducted to comprehensively evaluate the effects of factors that are known to influence residual chlorine wall decay constant such as water temperature, pipe diameter, initial chlorine concentration, and biofilm. Thus, this research was conducted to figure these issues out.

This study aimed at estimating wall decay constants of residual chlorine by performing lab tests along with estimation on bulk decay constants of residual chlorine in reclaimed water. Additionally, it was identified that the decay tendencies of residual chlorine concentration in the reclaimed water supply system, as well as the effects of water temperature, initial chlorine concentration, pipe diameter, and biofilm on wall decay constants.

2. Materials and methods

2.1. Mechanism of residual chlorine decay in water supply system

The decrease of residual chlorine in bulk water is caused by the chemical oxidation called as bulk decay reaction which refers to the consumption of residual chlorine occurred by organic compounds such as natural organic matter and inorganic substances including iron (II) and ammonia in bulk water, and natural decay due to volatilization as well.

Wable et al. [3] and Rossman et al. [4] revealed that the consumption of residual chlorine in the pipe for drinking water distribution system was significantly higher than that of in a non-reactive glass bottle. It means that there are other factors determining the consumption of chlorine in addition to chlorine decay in bulk water [3,4].

In water distribution systems, besides bulk decay reaction, there is the direct reaction between chlorine and pipe material or the reactions with accumulations such as the substances formed by corrosion of the pipe wall material, the biofilm formed on the pipe wall, and accumulated or absorbed organic compounds on the pipe wall; these are called as wall decay reaction. Its rate is affected by substances emitted from the pipe wall or attached at the pipe wall, and also affected by the rate of chlorine transfer from bulk water to reaction area of pipe wall [5].

Vasconcelos et al. [6] concluded that chlorine decay in a water distribution system was caused by reaction with pipe wall as well as reaction with bulk water. Fig. 1 shows the illustration of bulk decay reaction and wall decay reaction of residual chlorine in the water supply system [6].

Previous studies, using a first-order decay reaction model in analyzing chlorine decay, suggested that the affecting factors for wall decay constants were such as pipe material, pipe diameter, initial chlorine concen-

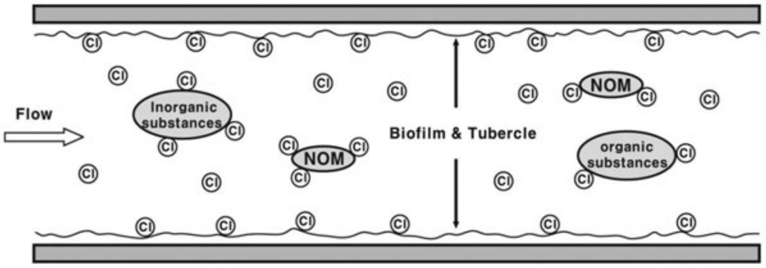


Fig. 1. Mechanisms of chlorine decay.

tration, water temperature, pipe corrosion rate, biofilm, and flow condition [2,5].

2.2. Test water sample and experimental apparatus

Reclaimed water collected from S reclaimed water treatment plant of I City in February 2012 was used for experiments. Reclaimed water in I City is produced by sand filtering, granular activated carbon filtering, and chlorination (sodium hypochlorite disinfection) using treated water which is discharged from the wastewater treatment plant, and is used for urban reuse such as toilet cleaning and road cleaning.

Water samples used for experiments were treated reclaimed water before chlorination, which was obtained at the sampling site and transported to the test lab for water quality analysis (water temperature was measured at the sampling site), and Table 1 shows the results.

The experiments were conducted to estimate wall decay constants in the test lab by using the reactor, where PVC pipes of diameters 77, 98, and 145 mm with 200 mm length between acrylic plates. Fig. 2 shows a schematic diagram of the reactor with PVC pipes for experiments to estimate wall decay constants. The reactor wall section consists of PVC pipes. The lower and upper cover of the reactor was made from acrylic material to minimize reaction with chlorine. An inlet valve to inject sample and an outlet valve for sampling were installed to the reactor. A magnetic stirrer was installed to the lower section of the reactor and the continuous mixing was done by inserting a magnetic stir bar inside the reactor.

Table 1
Water quality characteristics of sample

Parameter	Reclaimed water
Temperature (℃)	15.8–16.2
pH	6.84–6.93
Cl^- (mg/L)	1010.6
SO_4^{2-} (mg/L)	130.0
NH_3-N (mg/L)	1.4
NO_3-N (mg/L)	7.85
TOC (mg/L)	1.270
DOC (mg/L)	1.174
UV_{254} (abs./cm)	0.020
Hardness (as $CaCO_3$ mg/L)	420
Alkalinity (as $CaCO_3$ mg/L)	77
Cu (mg/L)	0.0231
Fe (mg/L)	0.0436
Mn (mg/L)	0.0413
Zn (mg/L)	0.0256

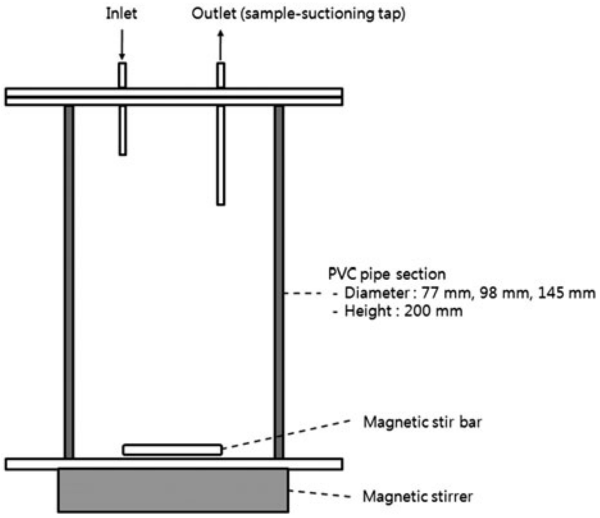


Fig. 2. Schematic diagram of the wall decay experimental apparatus.

2.3. Evaluation of residual chlorine decay constants

Total residual chlorine decay reaction in the supply system can be normally expressed with a first-order reaction model, where the first-order reaction occurring at the same time from both bulk water and pipe wall is included, respectively [5]. Total decay can be expressed as follows:

$$\frac{dC}{dt} = -k_t C = -(k_b + k_w)C = -\left(k_b + \left(\frac{S}{V}\right)K_w\right)C \tag{1}$$

where C = residual chlorine concentration in bulk at time t [ML^{-3}]; k_t = overall reaction constant or total decay constant [T^{-1}]; k_b = bulk water reaction constant or bulk decay constant [T^{-1}]; k_w = pipe wall solution reaction constant or effective wall decay constant [T^{-1}]; K_w = pipe wall surface reaction constant or inherent wall decay constant [LT^{-1}]; (S/V) = pipe inner wall surface area per unit volume of pipe [L^{-1}].

Given chlorine decay, decay relating to bulk water and decay relating to pipe wall are normally separated and considered, respectively. In Hua et al. [7] and AWWARF [8], total decay constant was defined as the sum of bulk decay constant and wall decay constant [7,8].

$$k_t = k_b + k_w \tag{2}$$

where k_t is defined as a first-order total decay constant, k_b is a first-order bulk decay constant, and k_w is a first-order wall decay constant. This model has advantages that it is comparatively simple and the mutual comparisons are easy with the use of the same unit (1/time) for decay constants [2]. k_w is calculated with the difference of k_t and k_b.

Among various first-order reaction models, this study adopted the exponential first-order decay model as the most suitable model and applied it to the quantification of residual chlorine decay [9].

$$C_t = a + b(e^{-k\cdot t}) \tag{3}$$

where the variable a represents the final residual chlorine concentration, the variable b the amount of the initial chlorine dose that reacts, in other words, $C_0 - a$. The variable k represents the residual chlorine decay constant and the variable t refers to time.

The chlorine disinfectant for experiments to estimate bulk decay constants and wall decay constants was sodium hypochlorite solution (NaOCl, 8%, Junsei). Bulk decay constants were calculated by the bottle test where free residual chlorine concentration was measured over time after sodium hypochlorite solution was injected into serum bottle, respectively, where water sample was inserted.

The experimental procedures to estimate wall decay constants are as follows: sodium hypochlorite solution was injected into water sample and they were mixed uniformly, and then, respectively kept stagnant in line at water temperature condition for 4 h considering average detention time before they were flown into the supply system after chlorine was dosed. The reactors were cleaned with distilled water after these were cleaned with sodium hypochlorite solution (about 1 mg/L), before experiments. Water sample which had been stagnant for 4 h after chlorine was dosed was put into the reactor and free residual chlorine concentration was measured by sampling through the outlet valve in the reactor according to the established measuring cycle. The measuring time was total 72 h. Table 2 shows the experimental conditions for wall decay constants.

Table 2
Experimental conditions of the pipe wall decay experiments

Parameter	Condition
Type of experiment	Batch test
Pipe material	PVC
Pipe diameter	77, 98, 145 mm
Temperature	5, 15, 25℃
Initial chlorine concentration	1, 2, 4 mg/L
Storage time	4 h
Stirring rate	100 rpm (average)

2.4. *Experiment on the wall decay reaction by the formation of biofilm*

Biofilm formation experiment for biofilm quantification was conducted by the following experimental conditions. PVC pipe reactor was used, and 98 mm of pipe diameter, 25℃ of water temperature, and 1 mg/L of initial chlorine concentration were given. And sodium hypochlorite solution was dosed to water sample then after 4 h water sample was flowed in the reactor to form biofilm. The reactors in which biofilm formed were taken out 3, 7, 11, 15, 19 d later (4 d intervals) and took biofilm formed on the pipe wall with a sterilized cell scraper and used for DNA quantitative analysis and the measurement of dry weight (DW).

The experiments for calculating the wall decay constants were proceeded using the reactors in which the biofilm were formed. The experimental conditions were water temperature as of 25℃, initial chlorine concentration as of 2 mg/L, and the measurement time was total 72 h.

2.5. *Analytical methods*

2.5.1. *Measurement of residual chlorine concentration*

N,N-diethyl-p-phenylenediamine colorimetric method was applied to measure the concentration of residual chlorine for understanding the tendency of residual chlorine decay. The free residual chlorine concentrations was measured using Pocket colorimeter™ II (Hach), which has the estimated detection limit of low range and high range of 0.02 and 0.1 mg/L, respectively.

2.5.2. *Bioflim quantification*

DNA extraction was conducted using phenol–chloroform extraction, and spectrophotometric method was applied to DNA quantification. The following shows the procedures of DNA extraction and quantification.

Cellulose acetate filters including filtered biofilm were freeze dried for 12 h. Freeze-dried filters were ground using liquid nitrogen. The powder of the filters and 1 mL DNA extraction buffer (200 mM Tris–HCl (pH 8.0), 20 mM EDTA (pH 8.0), 200 mM NaCl, RNaseA 10 μg/mL, ProtenaseK 10 μg/mL) were added to 2 mL e-tube. The 2 mL e-tube was incubated in the waterbath at 50℃. After 1 h, 20% SDS 400 μL was added to the sample within 2 mL e-tube. And then the 2 mL e-tube was incubated in the waterbath at 55℃. The e-tube was centrifuged for 5 min at 5,000 rpm and 25℃. The specific amount of supernatant liquids of the sample was taken and put into the new 2 mL e-tube and the same amount of phenol: chloroform (1:1) was added into the liquids. The e-tube with sample was shaken and incubated in the shaker for 1 h at 10 rpm. The e-tube was centrifuged for 15 min at 5,000 rpm and 25℃. The supernatant liquids of the sample was taken and put in new 2 mL e-tube and the same amount of SEVAG (chloroform: isoamyl alcohol (24:1)) was added into the liquids. After the e-tube with sample was shaken and incubated in the shaker for 1 h at 10 rpm, the e-tube was centrifuged for 15 min at 5,000 rpm and 25℃ again. The supernatant liquids of the sample were taken and put in new 2 ml e-tube and 60% (v/v) of IPA was added into the liquids. The e-tube with sample was incubated for 12 h at −20℃ and centrifuged for 15 min at 12,000 rpm and 4℃ after incubation. After the supernatant liquids of the sample were removed, 70% EtOH 1 mL was added. The e-tube was centrifuged for 10 min at 12,000 rpm and 4℃. The supernatant liquids were removed again and pellet finally obtained was dehydrated. DNA quantitation was conducted by UV–vis spectrophotometer (NanoDrop 2000, Thermo Scientific) after the dried pellet was dissolved in sterile distilled water.

2.5.3. Measurement of DW of biofilm

Samples including bioflim were filtered through predried cellulose acetate filters (porafil®, Macherey-Nagel) with a pore size of 0.2 μm in a vacuum filtration apparatus. The filters were lyophilized at −80℃ using Freeze dryer (Ilshin®). The difference between the filters lyophilized before and after filtration was DW.

3. Results and discussion

3.1. Effect of biofilm formation on wall decay constants

PVC pipes with a corrosion resistance are mainly used for the reclaimed water supply pipe. PVC pipes are strong against corrosion, and the dominant factors for wall decay reaction are considered to biofilm rather than corrosive matters. This experiment identified the actual tendency of biofilm formation in the supply pipe as a factor affecting wall decay constant, and it was calculated that wall decay constants through experiments after biofilm was formed in the reactor through the same process as the biofilm formation experiment.

Table 3 shows the amount of DNA per unit area in the pipe wall (ng/cm^2), DW of biofilm (mg), and inherent wall decay constant (K_w) over time. Basically, the amount of DNA is an index to identify the amount of living micro-organisms in the biofilm, and DW is an index to identify the amount of entire biofilm including organic matters, micro-organisms, and EPS among others. It was confirmed that the tendency of variations on the amount of DNA and DW over time was consistent with the tendency of variations on wall decay constants.

It can be understood that wall decay constants have a significant correlation with the amount of DNA through the correlation analysis between wall decay constants and the amount of DNA; between wall decay constants and DW (Pearson correlation coefficient $r = 0.883$, $p = 0.02$). From these results, it can be said that the amount of DNA is a more reliable index between the amount of DNA and DW as two indexes to quantify biofilm as a factor affecting wall decay constants.

Fig. 3 shows correlations between the amount of DNA and wall decay constant. If the amount of DNA increases, wall decay constant (m/d) increases as well. In case of the highest amount of DNA after 11 d from biofilm growth, its wall decay constant is 0.08328 m/d which is two times higher than wall decay constant when no biofilm exists (0.03927 m/d). Through this finding, it confirms that biofilm is the factor affecting wall decay constants.

3.2. Estimation of wall decay constants

All the experiments were carried out in a PVC pipe reactor where biofilm was formed for 10 d using

Table 3
DW, the amount of DNA, and inherent wall decay constant (K_w) over time after chlorination

Time (d)	DW (mg)	The amount of DNA per unit area (ng/cm^2)	K_w (m/d)
0	0	0	0.03927
3	2.1	5.624	0.0451
7	3.4	10.735	0.0661
11	17	54.924	0.08328
15	10.3	14.792	0.04135
19	17.8	45.812	0.09408

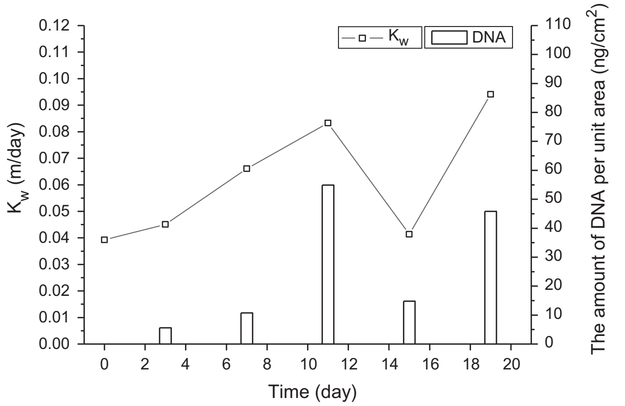


Fig. 3. The variation of inherent wall decay constant according to biofilm formation.

water sample where 1 mg/L of chlorine was dosed under 25℃ of water temperature in an effort to allow the same biofilm conditions. Free residual chlorine concentrations were measured depending on the measuring cycle after water samples with 1, 2, and 4 mg/L of chlorine were injected to the reactors where biofilm was formed, through which the estimation was made for bulk decay constant, total decay constant, and wall decay constant in the section from 4 h to the final 72 h after chlorination. The results are shown in the following Table 4.

As a result of experiments, the coefficient of determination (R^2) of a regression curve for the calculation of total decay constants and bulk decay constants showed high values to extent of 0.91–0.99, where the existence of wall decay could be confirmed other than bulk decay. The difference between total decay constants and bulk decay constants shows wall decay constant, through which k_w (h^{-1}) was calculated and showed 1.4–7 times of k_b (h^{-1}) at 1 mg/L of initial chlorine concentration. k_w was similar to k_b or showed values at maximum 3.5 times higher than k_b except for results from 7 out of 18 experimental cases even under 2 and 4 mg/L of initial chlorine concentration.

These findings are similar to those of Al-Jasser [10] and Hallam et al. [2] As a result of estimating wall decay constants in the PVC pipe from both studies, they showed values 5–10 times and 15 times higher than bulk decay constants, through which wall decay was confirmed to be superior in chlorine decay [2,10]. Similarly with these findings, wall decay is superior to bulk decay in chlorine decay in the reclaimed water supply system using PVC pipe where biofilm was formed, and it implies that a considerable amount of chlorine demand is consumed through wall decay. In addition, k_w was confirmed to be superior to k_b as initial chlorine concentration is lower with a smaller pipe diameter in addition to higher water temperature.

A inherent wall decay constant, K_w (m/d), was calculated by multiplying a hydraulic radius by an effective wall decay constant k_w (h^{-1}). The range of K_w under experimental conditions was minimum 0.012 m/d and maximum 0.20 m/d. It means that there was a great difference in K_w depending on water temperature, initial chlorine concentration, and pipe diameter although pipe material is same.

3.3. Effect of water temperature on wall decay constants

Most of the chemical reaction rate increases as temperature increases. As residual chlorine decay through wall decay reaction depends on chemical oxidation, chlorine decay reaction rate also increases when water temperature increases. There is Arrhenius equation as an experimental and empirical equation to express relationships between reaction rate constants and temperature in chemical reactions [7]. The variations of wall decay constant with water temperature can be expressed mathematically by Arrhenius equation:

$$k_w = Ae^{-(E/RT)} \tag{4}$$

where A = frequency factor (unit: equal to k_w); E = activation energy (kJ/mol); R = universal gas constant (8.3144 kJ/mol K); T = absolute temperature (K).

If natural logarithm is applied to Arrhenius equation above, the graph of natural logarithm of reaction rate constant against the reciprocal of absolute temperature can be plotted and the plotted graph is called Arrhenius plot. It can be seen that semi-logarithmic plot of Arrhenius equation is linear.

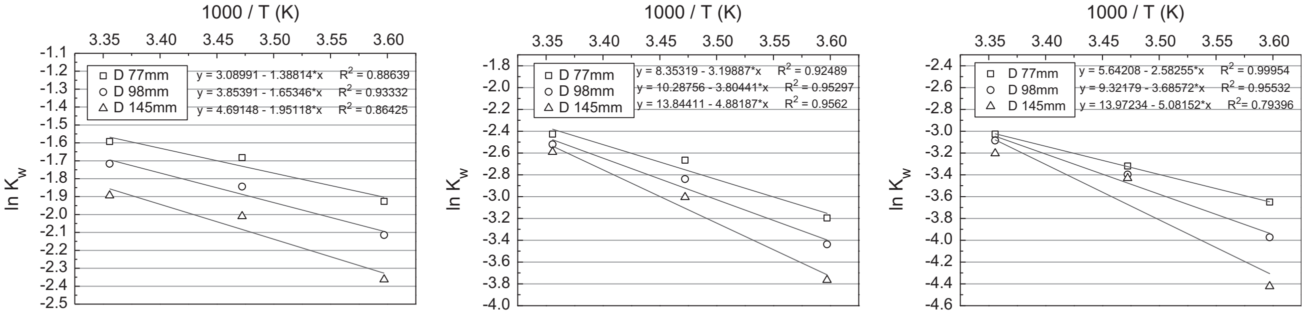
Figs. 4–6 show the results of 27 experimental cases presented in Table 4 and these figures have a certain signification because there are identical tendencies under each different condition of water temperature and initial chlorine concentration.

Fig. 4 shows correlations between water temperature and wall decay constants using Arrhenius plot. It is confirmed that wall decay constants increase as water temperature increases regardless of pipe diameter and initial chlorine concentration. The coefficient of determination (R^2) of linear regression equation under the rest of experimental conditions except for IC 4 mg/L, D 145 mm ranged from 0.85 to 0.99, implying that a considerable correlation exists between water temperature and wall decay constants. This is the same result as that of bulk decay constants. The increases of wall decay reaction rate according to the increase of water temperature lead to the increase of wall decay

Table 4
Effective wall decay constant (k_w) and inherent wall decay constant (K_w) by water temperature, pipe diameter, and initial chlorine concentration

lC (mg/L)	D (mm)	Temp. (℃)	k_t (h^{-1})	k_b (h^{-1})	k_w (h^{-1})	K_w (m/d)
1	77	5	0.38810	0.07277	0.31533	0.14568
		15	0.46605	0.06367	0.40238	0.18590
		25	0.50284	0.0627	0.44014	0.20335
	98	5	0.27804	0.07277	0.20527	0.12070
		15	0.33256	0.06367	0.26889	0.15811
		25	0.36822	0.0627	0.30552	0.17965
	145	5	0.18102	0.07277	0.10825	0.09418
		15	0.21767	0.06367	0.1540	0.13398
		25	0.23564	0.0627	0.17294	0.15046
2	77	5	0.16138	0.0728	0.08858	0.04092
		15	0.21336	0.06285	0.15051	0.06954
		25	0.24613	0.05497	0.19116	0.08832
	98	5	0.12749	0.0728	0.05469	0.03216
		15	0.16222	0.06285	0.09937	0.05843
		25	0.19160	0.05497	0.13663	0.08034
	145	5	0.09941	0.0728	0.02661	0.02315
		15	0.11979	0.06285	0.05694	0.04954
		25	0.14114	0.05497	0.08617	0.07497
4	77	5	0.10740	0.05116	0.05624	0.02598
		15	0.13105	0.05277	0.07828	0.03617
		25	0.16130	0.05641	0.10489	0.04846
	98	5	0.08314	0.05116	0.03198	0.01880
		15	0.10963	0.05277	0.05686	0.03343
		25	0.13406	0.05641	0.07765	0.04566
	145	5	0.06496	0.05116	0.0138	0.01201
		15	0.08993	0.05277	0.03716	0.03233
		25	0.10308	0.05641	0.04667	0.04060

Note: IC = initial chlorine concentration, D = pipe diameter, k_t = total decay constant, k_b = bulk decay constant, k_w = effective wall decay constant, K_w = inherent wall decay constant.



(a) IC 1 mg/L (b) IC 2 mg/L (c) IC 4 mg/L

Fig. 4. The relationship between water temperature and inherent wall decay constant.

constant. Hallam et al. [2] reported that wall decay reaction rate also increased due to the increase of water temperature which affected various parameters influencing on chlorine decay [2]. However, they could not prove correlations between water temperature and wall decay constants. Nevertheless, the findings from this study can explain the correlations between water temperature and wall decay constants.

3.4. Effect of initial chlorine concentration on wall decay constants

Fig. 5 shows a graph to show wall decay constants depending on initial chlorine concentration. Wall decay constants appear to decrease as initial chlorine concentration increases in each water temperature and pipe diameter. Many studies on relationships between wall decay constants and initial chlorine concentrations show results similar to these. According to various preceding studies, for example, including Kiene et al. [11] and Rossman [5], they suggested that wall decay reaction rate constant increases as initial chlorine concentration decreases [5,11]. AWWARF [8] reported that an inverse correlation existed similarly to bulk decay constants between wall decay constants and initial chlorine concentrations in a range from 0.3 to 5.0 mg/L of initial chlorine concentration [8]. Hallam et al. [8] reported that a strong inverse correlation existed between wall decay constants and initial chlorine concentrations as a result of estimating wall decay constants through field studies for PVC pipes, where a linear regression equation, $y = 0.26–0.73x$, could be obtained from a regression analysis results [2].

From previous study results and findings from this study, it could be explained that general chlorine decay reaction which includes wall decay reaction is actually not a first-order reaction and chlorine decay reaction can be affected by other reactants other than chlorine. Hua et al. [7] suggested that there might be another reactants' group other than residual chlorine. If this reaction is assumed to be a second-order reaction, a chemical reaction equation can be subsequently expressed in the following way [7]:

$$Cl_2 + \alpha X \Rightarrow P \tag{5}$$

$$\frac{dC}{dt} = -k_o(X_0 - \alpha C_0)C \tag{6}$$

where X = reactants; P = products; α = stoichiometry constant; C = residual chlorine concentration at time t; C_0 = residual chlorine concentration at time 0; k_o = overall reaction rate constant; X_0 = concentration of reactants at time 0.

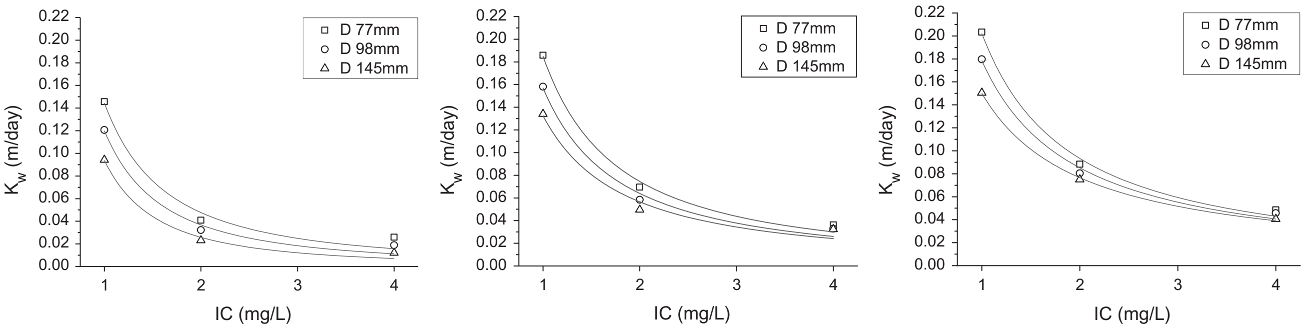
However, as residual chlorine decay reaction was assumed as a first-order reaction for this study, Eq. (6) is the same as the following Eq. (7) if it is expressed with a first-order reaction equation for C. Eq. (7) can be established under the assumption that the initial concentration of reactants (X_0) is higher than the initial chlorine concentration (C_0).

$$\frac{dC}{dt} = -k_1 C \tag{7}$$

$$k_1 = -k_o(X_0 - \alpha C_0) \tag{8}$$

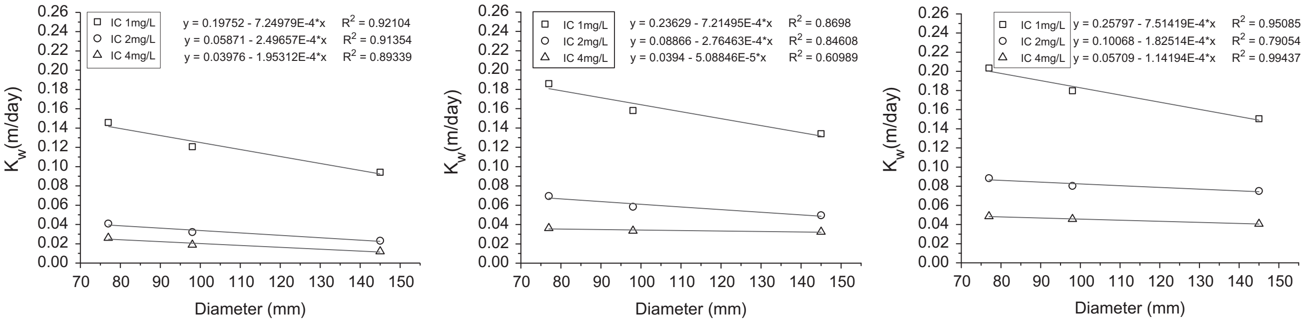
The first-order reaction rate constant, k_1 is actually a function of initial chlorine concentration, C_0, as shown in Eq. (8), and k_1 will increase if initial chlorine concentration decreases under the condition that the concentration of other reactants, X_0, does not change [5]. This is why chlorine decay constants tend to decrease according to the increased initial chlorine concentration when residual chlorine decay reaction is expressed in a first-order decay model [7]. In other words, bulk decay constant or wall decay constant obtained from this research is the first-order reaction rate constant, which is a function of initial chlorine concentration. Consequently, residual chlorine decay constants decrease as initial chlorine concentrations increase.

In addition, the decrease of wall decay constants shows similar patterns under all of water temperature



(a) Temp. 5 ℃ (b) Temp. 15 ℃ (c) Temp. 25 ℃

Fig. 5. The relationship between initial chlorine concentration and inherent wall decay constant.



(a) Temp. 5 ℃ (b) Temp. 15 ℃ (c) Temp. 25 ℃

Fig. 6. The relationship between pipe diameter and inherent wall decay constant.

and pipe diameter. Especially in IC 1–2 mg/L, wall decay constants decrease greatly while the decreasing gap declines gradually. The linear regression analysis between wall decay constants and initial chlorine concentration was carried out. However, the coefficient of determination (R^2) of the linear regression equation was shown to the extent of 0.36–0.69. This coefficient of determination implies that the linear function does not perfectly explain the relationship between two variables.

As a result of regression analysis with a power function instead of linear regression analysis, all the coefficients of determination are 0.95 or higher, which is optimal.

These findings are very similar to the experimental results by Hallam et al. [2]. Hallam et al. [2] indicated that a power function was more suitable than a linear function for regression analysis between wall decay constant and initial chlorine concentration through experiments using PVC, cement lined cast iron, and MDPE pipes [2]. The fact that wall decay constants decrease as initial chlorine concentrations are higher and a power function is applied instead of a linear function between initial chlorine concentrations and wall decay constants implies that there is limited rate in reaction between chlorine and pipe wall.

3.5. Effect of pipe diameter on wall decay constants

Fig. 6 shows the graphs in the linear regression for relationship between pipe diameter and inherent wall decay constant (K_w) by water temperature. The coefficient of determination (R^2) of the linear regression equations shows high values in 0.85–0.99 except for the cases of water temperature at 25℃ and IC 2 mg/L, and water temperature at 15℃ and IC 2 mg/L. The values of the slope of regression equation are negative. Through these findings, it is confirmed that a considerably negative correlation exists between pipe diameter and wall decay constant. In other words, the increase of pipe diameter is led to the decrease of wall decay constant. In addition, relationship between two variables, pipe diameter and wall decay constant, can be expressed in a linear equation and wall decay constants at other pipe diameters can be estimated as well.

In derived results of effective wall decay constant (k_w) per unit area of the pipe inner wall, wall decay constant (k_w) per unit of inner area at 77 mm of pipe diameter under 1 mg/L of initial chlorine concentration is 0.016–0.022 d^{-1} cm^{-2}, which is about 4–5 times larger than 0.003–0.005 d^{-1} cm^{-2} at 145 mm of pipe diameter. It can be confirmed that the smaller pipe diameter promotes chlorine reaction and speed up the chlorine consumption rate per unit area of pipe inner wall. Lee et al. [12] reported that variations in pipe diameter showed clear differences in wall decay constants as chlorine decay constants of a 50 mm diameter of metallic pipe showed values about twice higher than those of an 80 mm diameter of metallic pipe [12].

It is considered that major causes to increase wall decay reaction rate are the increase of the opportunity for contact between chlorine in the bulk water and pipe inner wall, and the increase of effective interfacial area resulting from the decrease of pipe diameter.

4. Conclusions

This study aimed at evaluating the decay tendency of residual chlorine concentration for the reclaimed water supply system which currently supplies urban reclaimed water. The experiments to estimate residual chlorine wall decay constants in total 27 sets were carried out depending on water temperature, initial chlorine concentration, and pipe diameter. In addition, the experiments to estimate the effects of biofilm formation on residual chlorine decay constants for the reclaimed water supply system were carried out. The conclusions derived from those experiments are as follows:

(1) As a result of experiments for the biofilm formation using PVC pipe reactors, the biofilm formation in the reactor where chlorinated reclaimed water was injected was confirmed through the amount of DNA per unit area (ng/cm^2) and DW (mg). An increase in the amount of biofilm leads to the increase of residual chlorine wall decay constants. The wall decay constant after 11 d from the biofilm formation to show the highest amount of DNA was 0.083 m/d which showed a difference of twice or more than 0.039 m/d for the wall decay constant without any biofilm formation.

(2) As a result of confirming the effects of water temperature on wall decay constants, the residual chlorine decay reaction rate increases as water temperature increases because residual chlorine decay reaction belongs to chemical oxidation. For such a reason, wall decay constants tend to increase.

(3) As a result of confirming the effects of initial chlorine concentration on wall decay reaction, wall decay constants were higher in lower initial chlorine concentrations regardless of water temperature and pipe diameter. Through these findings, chlorine decay reaction was assumed as a first-order reaction but it was not actually a first-order reaction. It proves that other groups of reactants exist and cause residual chlorine decay as they react with chlorine.

(4) As a result of confirming wall decay constants depending on pipe diameter, the increase of pipe diameter is led to the decrease of wall decay constants. The effective wall decay constant (k_w) per unit area at 77 mm of pipe diameter under 1 mg/L of initial chlorine concentration is about 4–5 times larger than that at 145 mm of pipe diameter, through which it is confirmed that smaller pipe diameter is led to faster residual chlorine consumption rate per unit area of pipe inner wall. The increase of the opportunity of contact between residual chlorine in bulk water and pipe inner wall, and the increase of effective interfacial area due to the decrease of pipe diameter are considered to be the causes of increase of wall decay reaction rate.

The results of this research could be used for the database for predictive modeling of residual chlorine concentration in reclaimed water supply system. Moreover, these results of this study is available as fundamental data to calculate optimal chlorine demand for maintaining proper residual chlorine concentration in reclaimed water supply system.

Acknowledgements

This study was supported by the main project “Development of Water Distribution Technology in Microgrid” of Korea Institute of Construction Technology.

References

[1] H. Ryu, A. Alum, K.D. Mena, M. Abbaszadegan, Assessment of the risk of infection by Cryptosporidium and Giardia in non-potable reclaimed water, Water Sci. Technol. 55(1–2) (2007) 283–290.

[2] N.B. Hallam, J.R. West, C.F. Forster, J.C. Powell, I. Spencer, The decay of chlorine associated with the pipe wall in water distribution systems, Water Res. 36 (14) (2002) 3479–3488.

[3] O. Wable, N. Dumoutier, J.P. Duguet, P.A. Jarrige, G. Gelas, J.F. Depierre, Modeling chlorine concentrations in a network and applications to Paris distribution network, in: Proceedings of Water Quality Modeling in Distribution Systems Conference, AWWA Research Foundation, OH, 1991, pp. 77–87.

[4] L.A. Rossman, R.A. Brown, P.C. Singer, J.R. Nuckols, DBP formation kinetics in a simulated distribution system, Water Res. 35(14) (2001) 3483–3489.

[5] L.A. Rossman, The effect of advanced treatment on chlorine decay in metallic pipes, Water Res. 40(13) (2006) 2493–2502.

[6] J.J. Vasconcelos, L.A. Rossman, W.M. Grayman, P.F. Boulos, R.M. Clark, Kinetics of chlorine decay, J. Am. Water Works Assoc. 89(7) (1997) 54–65.

[7] F. Hua, J.R. West, R.A. Barker, C.F. Forster, Modelling of chlorine decay in municipal water supplies, Water Res. 33(12) (1999) 2735–2746.

[8] AWWARF, Characteristics and Modelling of Chlorine Decay in Distribution Systems, AWWA, Denver, CO, 1996.

[9] B. Warton, A. Heitz, C. Joll, R. Kagi, A new method for calculation of the chlorine demand of natural and treated waters, Water Res. 40(15) (2006) 2877–2884.

[10] A.O. Al-Jasser, Chlorine decay in drinking-water transmission and distribution systems: Pipe service age effect, Water Res. 41(2) (2007) 387–396.

[11] L. Kiene, W. Lu, Y. Levi, Parameters governing the rate of chlorine decay throughout distribution system, in: Proceedings of the AWWA 1993 Annual Conference, CO, 1993.

[12] H.D. Lee, W.S. Chung, P.J. Kwak, M.K. Kim, Behavior of chlorine residual in waterworks system, in: Proceedings of the KSWE-KSWW-KWWA Joint Conference, Seoul, Republic of Korea, 2000, pp. 169–172.