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Application of corrosion inhibitors to water distribution systems

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The current study evaluated the disinfection efficiency of free chlorine and chloramine for microorganisms on various pipe materials, such as copper, galvanized steel, carbon steel, and stainless steel. In addition, the effect of internal pipe corrosion and corrosion inhibitors on the bactericidal efficiency was evaluated using a simulated loop. For disinfection with a phosphate corrosion inhibitor, chloramination was found to be more effective than chlorination due to its persistence. Free chlorine disinfection was optimized with a high phosphoric acid concentration, while chloramine disinfection was optimized with a high phosphoric acid or low polyphosphate concentration. In simulated copper and galvanized steel loop tests, chloramination with phosphoric acid was demonstrated to be more effective.

Key words : chloramination, disinfection, inhibitor, corrosion, distribution system

1. Introduction

The various problems related to distribution systems, such as DBPs, which are produced when using free chlorine, the regrowth of pathogenic microorganisms, corrosion, which causes red water, tastes, and odors, can be more effectively understood by evaluating the interrelationships of microorganisms, disinfectants, and corrosion. In managing distribution systems, chloramination would appear to be successful for corrosion control and the efficient disinfection of attached microorganisms, which can be a source of an outbreak of pathogenic bacteria.

Corrosion is the primary process that reduces chlorine residuals. The relationship between the corrosion rate and the disinfection efficiency of free chlorine follows an exponential curve, indicating that a small increase in the corrosion rate dramatically reduces the effectiveness of the free chlorine disinfection of biofilm bacteria. However, free chlorine also exhibits a linear relationship to the corrosion rate, plus, due to its high reaction rate, free chlorine is largely consumed before it penetrates the biofilm. In contrast, monochloramine is more limited in the types of compounds with which it will react, therefore, it is expected that monochloramine may have a better ability to penetrate the biofilm layer and inactivate attached organisms[1,2].

The application of corrosion inhibitors(polyphosphate, zinc ortho-phosphate, or pH and alkalinity adjustment) has been used to improve the disinfection efficiency of free chlorine for biofilm bacteria[3~5], indicating that reducing the corrosivity of the water may improve the disinfection of biofilm organisms.

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It is likely that biofilm organisms combine ferrous ions from the metal surfaces within the glycocalyx layer. Free chlorine not only reacts with extracellular polysaccharides but also liberates ferrous ions, which consume the chlorine residual. However, since monochloramine does not react with capsular materials, the disinfectant is available for the inactivation of biofilm organisms[1]. When the application of corrosion inhibitors(polyphosphate, zinc ortho- phosphate, or pH and alkalinity adjustment) was used to improve the disinfection efficiency of free chlorine for biofilm bacteria in iron pipes[3,4], the results suggested that corrosion may have been related to the occurrence of coliform bacteria in the Seymour, Ind., distribution system as the coliform level decreased within a few weeks after the application of zinc orthophosphate. Martin *et al.*[5] reported that adding lime to treated water supplies was an effective method of pH and bacterial control.

Based on these previous reports, which indicate that reducing the corrosivity of water improves the free chlorine disinfection of biofilm organisms, the current study proposes the application of chloramine and a phosphate corrosion inhibitor to reduce corrosion and facilitate biofilm control. Although phosphate corrosion inhibitors can decrease the corrosion rates of internal pipe surfaces, they are also a source for microorganism utilization, resulting in an increase of microorganisms. In various other studies[3,4], the microorganisms in distribution systems were decreased by an injection of a corrosion inhibitor. When a phosphate corrosion inhibitor is injected for corrosion control, the appropriate disinfectant is also needed. Therefore, the use of Chloramine as a secondary disinfectant may be effective due to its persistency. In addition, the proper ratio for the disinfectant and corrosion inhibitor concentrations must also be determined to optimize the corrosion control and disinfection process. Accordingly, the current study was conducted to evaluate the effect of phosphate corrosion inhibitors on the disinfection efficiency of free chlorine and chloramine.

2. Experimental

The present study was conducted to evaluate the disinfection efficiency of free chlorine and chloramine for microorganisms suspended or attached to various pipe materials. such as copper, galvanized steel, carbon steel, and stainless steel. The effect of internal pipe corrosion and corrosion inhibitors on the bactericidal efficiency was also evaluated using a simulated loop.

2.1 Materials

2.2.1 Corrosion inhibitors

The inhibitors used in the experiments were ortho-phosphate(H_3PO_4) and commercial ploy-phosphate. To prepare stock solutions, phosphoric acid was diluted to 1000 mg P/L and polyphosphate was dissolved and diluted to 1000 mg P/L. The phosphate concentration was measured periodically to ensure the same concentration.

2.1.2 Control water

Control water was prepared as a comparison for the corrosion resulting from the disinfectant and attached microorganisms. The control water was adjusted to pH 7 with 0.2 N KOH, an alkalinity of 50 mg $CaCO_3$/L using H_2CO_3, and calcium hardness of 50 mg $CaCO_3$/L using $CaCl_2$.

2.1.3 Inoculated BOD solution

The test sample for most experiments was an inoculated BOD solution, which included a carbon source made with glucose and glutamic acid 50:50 to make 3 mg C/L and adjusted to pH 7 with a buffer solution. This sample was inoculated at a constant volume(1 % V/V), while the protozoa were removed by means of filtering the surface water with Whatman No. 42 filter paper(pore size 2.5 ㎛).

2.1.4 Sleeve and coupon

The sleeves were made of acrylic plastic in the shape of a cylinder, 20 mm diameter, 400 mm length, which allowed the insertion of 5 pipe coupons. The quick-fit sleeves provided easy access to the interior of the pipe coupons for analysis of the biofilm populations. The coupons were made with copper, galvanized steel, or carbon steel.

2.2 Experimental Methods

2.2.1 Suspended microorganisms

The microorganisms suspended in the samples were measured as HPC. The collected samples

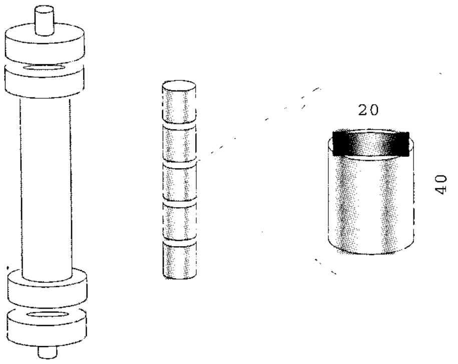


Fig. 1. Schematic of sleeve and coupons.

of suspended microorganisms were dechlorinated by 0.1N $Na_2S_2O_3$. The HPC bacteria were then enumerated in duplicate using the spread plate technique with R2A media and incubation at 20 ℃ for 7 days.

2.2.2 Attached microorganism

To prepare samples of the microorganisms attached to the coupons of various pipe materials, each coupon from sleeves was collected and rinsed three times with a phosphate buffer solution(10 mM, pH 7.2). The rinsed coupons were then immersed in 150 mL of a BOD dilution solution and sonicated at 40 W for 2 minutes using sonication equipment(Sonics & Materials Inc. Model VCX 400) to separate the attached microorganisms from the coupon interior surface. The separated microorganisms were then enumerated in duplicate using the spread plate technique with R2A media and incubation at 20 ℃ for 7 days.

2.2.3 Corrosion

A weight-loss analysis was conducted to provide an indication of the corrosion rate over the exposure period. The collected coupons were immersed in a constant water volume and sonicated for 1 hour using the sonication equipment. The sonicated coupons were rinsed several times with distilled water and then dried in a dry oven for 24 hours. The coupons were weighed 3 times using a mass balance. The coupon weight was decided as the mean value. In each experiment fresh coupons were prepared to evaluate the corrosion under the same conditions.

2.2.4 Simulated Loop Test

Simulated pipe loops(Figure 2) were constructed to test the application of the disinfectants and corrosion inhibitors. The model system was composed of an approximately 6m-long pipe section and 5 L mixing tank. Copper and galvanized steel pipes with interior diameters of about 2 cm were used for the test.

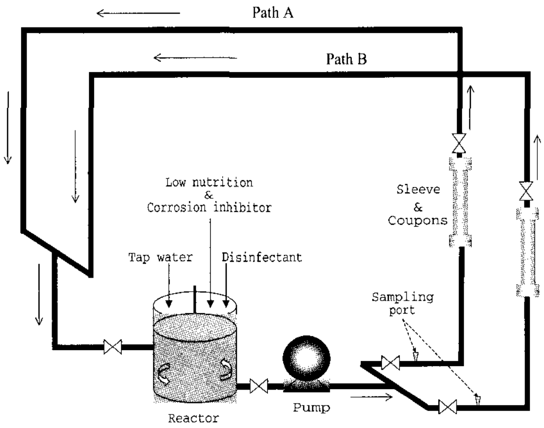


Fig. 2. Schematic of simulated loop system.

As described in Table 1, the flow velocity and pressure of the water in the pipes were maintained at 0.3 m/sec and 0.4~0.5 kg_f/cm^2, respectively. To avoid a temperature increase due to friction between the pipe surface and the water flowing through it, Path A and Path B were opened/closed in turn every hour. The system was operated for 12 hours a day. After a 2-day growing period using the inoculated BOD solution, an accommodation

Table 1. Characteristics of the simulated loop

	Parameters		Value
Water sample (tap water)	pH		7.3
	Alkalinity(mg$CaCO_3$/L)		48
	DOC(mgC/L)		0.85
	Total chlorine(mgCl_2/L)		0.15
	Free chlorine(mgCl_2/L)		0.08
Physical characteristics	Loop tube length(m)		about 6
	Volume(L)	Loop	4.3
		Total	9.3
	Wetted surface area(cm^2)		3770
	Pressure(kg_f/L)		0.4~0.5
Hydraulic characteristics	Water flow velocity(m/s)		about 0.3
	Retention time(hrs)		3.1

period was implemented with only tap water and a low-nutrient mixture at a rate of 45 mL/min and 5 mL/min, respectively.

The low-nutrient mixture, consisting of 1.0 mg glucose, 0.7 mg K_2HPO_4, 0.3 mg KH_2PO_4, 0.01 mg $MgSO_4 \cdot 7H_2O$, 0.01 mg$(NH_4)_2SO_4$, 0.01 mg NaCl, 1.0 μg $CaCl_2$, and 0.1 μg $FeSO_4$(per liter, injection concentration), was added to the mixing tank using a digital peristaltic pump. This low-nutrient formulation had been previously shown to enhance microbial resistance to disinfection[6]. After the accommodation period, 30 mgP/L of H_3PO_4 or polyphosphate as the corrosion inhibitor and the low-nutrient mixture were pumped into the mixing tank at a rate of 5 mL/min. Meanwhile, 30 mg of Cl_2/L free chlorine or chloramine as the disinfectant was also pumped into the mixing tank using another peristaltic pump at a rate of 5 mL/min. Tap water was injected at a rate of 40 mL/min by means of an adjusting flow meter. The ideal inhibitor and disinfectant concentrations in the system were 3 mgP/L and 3 $mgCl_2$/L respectively.

Before injecting the inhibitor and disinfectant, 5 coupons were collected from the sleeves to analyze the attached microorganisms and weight-loss, plus samples to determine the suspended microorganisms were also collected from the sampling ports. After 10 days the other 5 coupons were analyzed using the same method to calculate the disinfection efficiency and weight-loss. The phosphate and free/total chlorine residual were measured every day.

3. Results and Discussion

3.1 Effects of Phosphate Corrosion Inhibitors on Disinfection Efficiency

3.1.1 Disinfection Efficiency According to Dose of Phosphate Inhibitor

Figures 3 and 4 present the viable HPCs when the disinfectants were injected at a concentration of 1 $mgCl_2$/L. When phosphoric acid was injected, the disinfection efficiency of chloramine was better than that of free chlorine with a 10-hour contact time. Although the increase in HPCs was faster when using chloramine than with free chlorine, the final HPC count was less with chloramine, possibly because the chlorine residual of chloramine was more persistent.

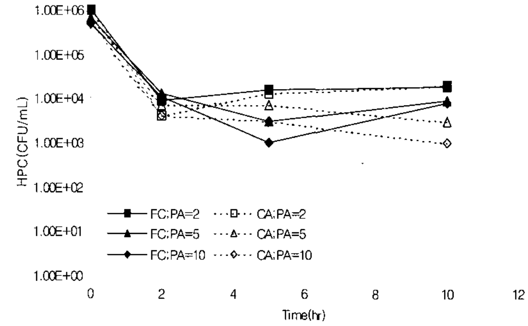


Fig. 3. Counts of HPCs according to phosphoric acid concentration with 1 $mgCl_2$/L disinfectants.

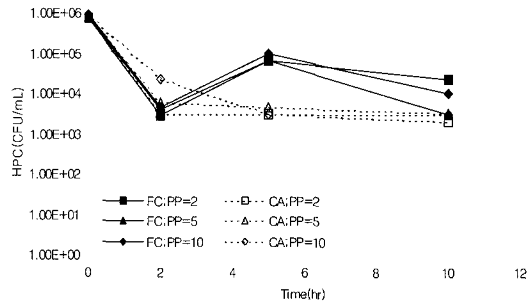
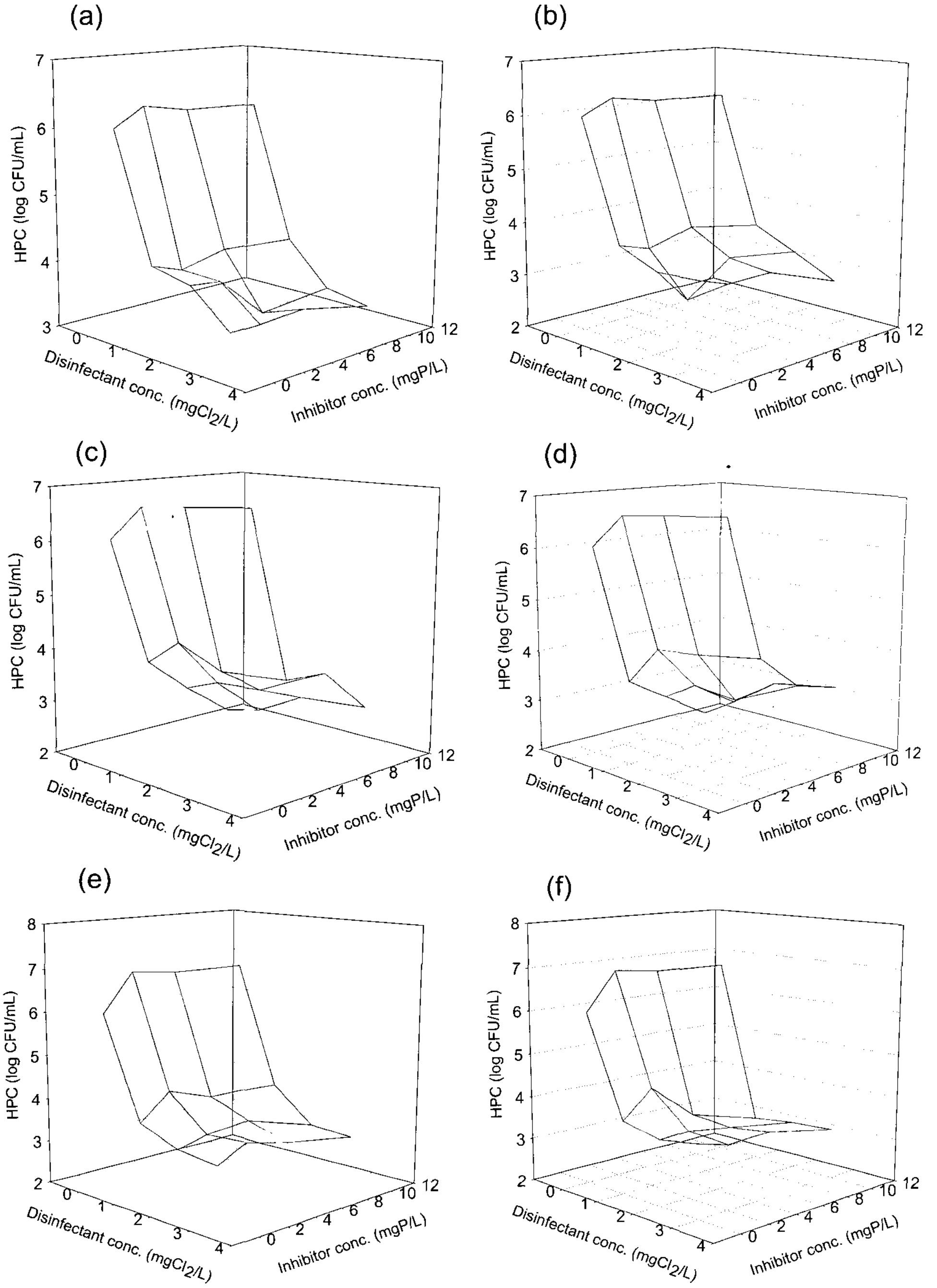


Fig. 4. Counts of HPCs according to polyphosphate concentration with 1 $mgCl_2$/L disinfectants.

When polyphosphate was injected, the disinfection efficiency of free chlorine was similar orsuperior to that of chloramine for the first 2 hours. However, after 2 hours, chloramine became more effective than free chlorine due to its higher chlorine residual. The HPC count when using free chlorine increased dramatically during 2~5 hours and thereafter decreased. This may have been due to the exhaustion of the chlorine residual of free chlorine and nutrients utilized by the microorganisms. Therefore, for disinfection with a phosphate corrosion inhibitor, the persistence of chloramination was clearly more effective than chlorination.

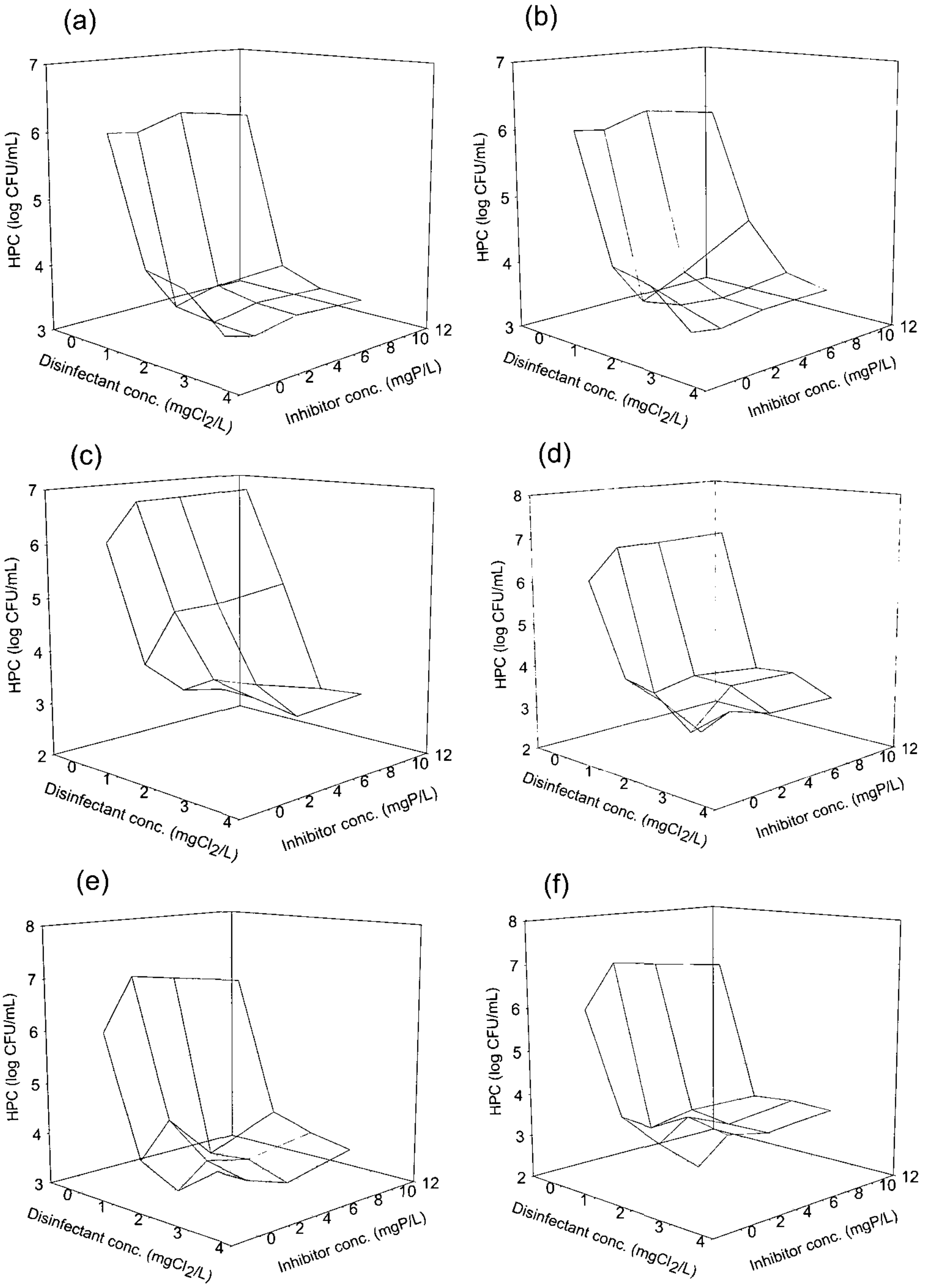
3.1.2 Disinfectant/Inhibitor ratio

The HPC counts according to the ratio of the free chlorine or chloramine concentration to the phosphoric acid or polyphosphate concentration are shown in Figures 3 and 4. These results reveal the phosphate inhibitor concentration with the



	Contact time(hr)		
	2	5	10
Free chlorine	(a)	(c)	(e)
Chloramine	(b)	(d)	(f)

Fig. 5. Viable counts of HPCs according to disinfectant and phosphoric acid (inhibitor) concentrations.



	Contact time(hr)		
	2	5	10
Free chlorine	(a)	(c)	(e)
Chloramine	(b)	(d)	(f)

Fig. 6. Viable counts of HPCs according to disinfectant and polyphosphate(inhibitor) concentrations

Table 4. Disinfection efficiencies with the optimum rate of disinfectants and phosphate corrosion inhibitors

		A(B) A= Maximum disinfection efficiency(%) B= Optimum inhibitor Concentration according to each disinfectant concentration(mgP/L)					
		Phosphoric acid			Polyphosphate		
		2 hr	5 hr	10 hr	2 hr	5 hr	10 hr
Free chlorine ($mgCl_2/L$)	1	99.08(2)	99.84(10)	99.40(0)	99.71(2)*	98.98(0)*	99.53(5)*
	2	99.69(5)	99.67(10)	99.80(10)*	99.76(2)*	99.83(10)*	99.74(0)
	3	99.70(10)	99.89(10)*	99.82(10)*	99.77(2)*	99.83(5)	99.67(5)
Chloramine ($mgCl_2/L$)	1	99.59(2)	99.53(10)	99.84(10)*	99.69(2)*	99.69(2)*	99.80(2)
	2	99.92(2)*	99.81(10)	99.80(10)*	99.49(5)	99.94(2)*	99.74(0)
	3	99.89(10)*	99.73(10)	99.77(10)	99.73(2)	99.78(0)*	99.86(0)*

: greater disinfection efficiency between use of free chlorine and chloramine

* : greater disinfection efficiency between use of phosphoric acid and polyphosphate

greatest disinfection efficiency, plus the lowest points for each disinfectant concentration, also described in Table 2.

When phosphoric acid was injected(Figure 5), in most cases the phosphoric acid concentration with the lowest HPC count was 10 mgP/L relative to time when using free chlorine or chloramine. Here, the disinfection efficiency may have been affected by the pH resulting from an injection of phosphoric acid.

In contrast, when polyphosphate was injected (Figure 6), the minimum HPC counts were mostly found with 2 mg P/L polyphosphate within 2 hours of contact when using free chlorine or chloramine. The minimum points after 2 hours of contact were 0 or 2 mgP/L with chloramine, however, no pattern was exhibited with free chlorine.

In conclusion, the free chlorine disinfection was optimized with a high phosphoric acid concentration(low concentration ratio of disinfectant to phosphoric acid), while the chloramine disinfection was optimized with a high phosphoric acid or low polyphosphate concentration(low concentration ratio of disinfectant to phosphoric acid or high concentration ratio of disinfectant topolyphosphate).

3.1.3 Simulated Loop Test

The disinfection efficiencies of free chlorine and chloramine for suspended/attached microorganisms with/without phosphoric acid in a simulated loop system are described in Figure 7.

In all cases, disinfection with phosphoric acid was more effective. It would appear that the injection of phosphoric acid decreased the pH in the system, thereby increasing the disinfection ability. However, since there was also a decrease in the corrosion, this may have increased the consumption of the disinfectant and resulted in more microorganism sites becoming inaccessible to the disinfectant.

Previous studies by Le Chevallier *et al.*[3] and Lowther & Moser[4] also showed that corrosion inhibitors can decrease the population of biofilm bacteria by reducing corrosion, the products of which protect biofilm bacteria from disinfectants.

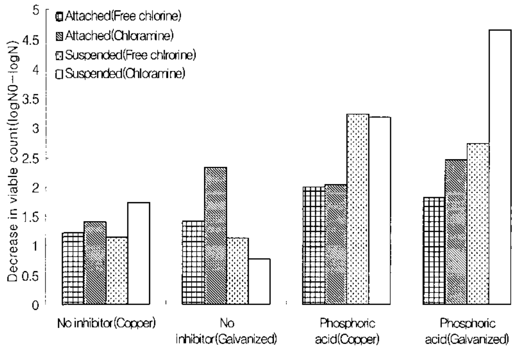


Fig. 7. Disinfection efficiencies of free chlorine and chloramine for suspended/attached microorganism with/without phosphoric acid in simulated loop system.

The disinfection efficiencies of chloramination and chlorination with phosphoric acid in a copper pipe were similar for suspended and attached microorganisms, however, in galvanized steel, chloramine was more effective than free chlorine for both suspended and attached microorganisms. This may have been because the accumulation of the corrosion products of galvanized steel provided rougher surfaces than with copper. The corrosion products were considered to be $Zn(OH)_2$ and ZnO (ILZRO 1967), which are whitish and fragile, plus their surfaces are rough. Therefore, chloramine was found to be more effective than free chlorine due to its penetrative ability.

4. Conclusions

The current study focused on the interrelationships between attached/suspended microorganisms, free chlorine/chloramine, and the corrosion of various pipe materials. The main purpose was to evaluate the effects of chloramine as a secondary disinfectant on disinfection efficiency and the corrosion of pipe materials as a means of controlling biofilm within a relatively short time period. The main conclusions were as follows :

For disinfection with a phosphate corrosion inhibitor, chloramination was found to be more effective than chlorination due to its persistence. Free chlorine disinfection was optimized with a high phosphoric acid concentration, while chloramine disinfection was optimized with a high phosphoric acid or low polyphosphate concentration. In simulated copper and galvanized steel loop tests, chloramination with phosphoric acid was demonstrated to be more effective.

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