Asian Journal of Chemistry Vol. 20, No. 7 (2008), 5745-5759

Corrosion Control by using $Ca(OH)_2$ and CO_2 in Water Distribution Systems

DONGCHAN LEE†, YOONJIN LEE* and SANGHO NAM‡
Department of Environmental Engineering, Cheongju University, 36, Naedok-dong
Sangdang-gu, Cheongju, Chungbuk, 360-764, Republic of Korea
E-mail: yjlee@cju.ac.kr

This study was performed to evaluate the application of controlling methods for corrosive water quality in water supply systems. Among the chemicals $Ca(OH)_2$, $NaHCO_3$, NaOH and Na_2CO_3, $Ca(OH)_2$ were the most effective for controlling alkalinity, pH and calcium concentration in the supplied water. The level of Fe, Zn and Cu in non-treatment pipes appeared to be 1.3, 1.4 and 1.4 times higher than conditions treated with $Ca(OH)_2$ and CO_2 in carbon steel, galvanized steel, copper pipe plumbing systems, respectively. The corrosion rate was effectively decreased with the treatment of $Ca(OH)_2$ and CO_2 in the pipe systems. The main components of the scale layer were iron and zinc which were 95.9 and 89.2 % for carbon steel and galvanized pipes in the $Ca(OH)_2$ and CO_2 treated pipe system, respectively. The substance of calcium in the layer was analyzed to be about 1.9, 1.1 % for carbon steel and galvanized pipes with the treatment of $Ca(OH)_2$ and CO_2.

Key Words: Corrosion control, Water distribution system, Pipe, $Ca(OH)_2$-CO_2 process.

INTRODUCTION

Problems can occur such as red coloured water and turbid water, taste and odor and the release of metal substances into tap water by corrosion in water distribution systems[1]. It can bring economical loss by water leakage and reduction of the pipe life time due to decreasing wall thickness and pipe material damage[1-5].

Corrosion was defined by ISO as physico-chemical interactions between a metal and its environment which results in changes in the properties of the metals[6]. There are various types of corrosion such as galvanic corrosion, crevice corrosion, pitting, intergranular corrosion, erosion corrosion[7]. The corrosion phenomenon is influenced by physical factors such as temperature and water velocity and chemical factors such as pH, Cl^- and dissolved oxygen[8].

---

†Material Evaluation Team, Korea Testing and Research Institute, Gomak-ri, Worlgot-myeon, Gimpo-si, Gyeonggi-do, 415-871, Korea.

‡Department of Environmental Engineering, Konkuk University, 1, Hwayang-dong, Gwangjin-gu, Seoul, 143-701, Korea.

The problems of corrosion and superannuation for the water distribution system in Korea should occur since surface water quality in Korea is generally estimated to be corrosive, low alkalinity water[9]. Kwak *et al.*[4] reported the Langelier Index (LI) to be negative values and the Larson Ratio (LR) was over 0.7 for the Han river.

There are the corrosion control and management methods of water quality adjustment such as pH and alkalinity, use of corrosion inhibitors, replacement of old pipes and so on in water distribution systems[10-17]. The control methods of water corrosiveness by adjustment of pH and alkalinity are regarded as economical methods to apply with supplied water[18]. Generally, suitable pH ranges to control corrosion are reported between 6.5 and 8.5 for tap water[8,12,13]. However, the corrosion continued up to a pH of 8.5 while the condition of alkalinity was distinctly low and a high level of ionic materials existed[12,13]. The chemical Na_2CO_3 was successfully used to protect from copper pitting failures in resident plumbing systems in the Highland Greens subdivision of Fort Shawnee, Ohio[13]. The case of Seattle, Washington is regarded as a good case to solve copper corrosion problems by increasing pH, alkalinity with lime and soda ash[13].

This research evaluated the variation of corrosion velocity and water variables while applying $Ca(OH)_2$ and CO_2 to the supplied water, which tested as corrosive water by LI(-1.9) and RI(10.8) inside the Konkuk University, located in Seoul metropolitan city. In this research to evaluate the application potentiality of $Ca(OH)_2$ and CO_2 for controlling corrosive water quality, the pipe systems consisted of carbon steel, galvanized iron steel, copper pipe.

EXPERIMENTAL

The schematic diagram of pipe systems in this research is presented in Fig. 1. The total pipe length was 7.4 m and the water velocity was 1.0-1.2 m/s. The pipe systems were composed of carbon steel, galvanized, copper pipe to compare influences of pipe materials. Coupon systems were installed in 10 cm section intervals of carbon steel, galvanized, copper pipe joined with quick-fit PVC coupling for analysis of corrosion velocity and SEM (scanning electronic microscopy). The system was attached to a real time measuring pH meter, conductivity meter and DO meter. The levels of Fe, Zn, Cu were measured by ICP (inductively coupled plasma spectroscopy, Labtem 8440). In addition, each coupon was pretreated with outside coating to block the effects of outside air before installation on pipe systems. This circulation pipe system was operated for 2 h after which the running was paused and after the feed water was changed, it was operated again. The coupons were eliminated at the set time of 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55 and 60 d. The weight differences between the initial and set reaction time were measured to determine the corrosion velocity.

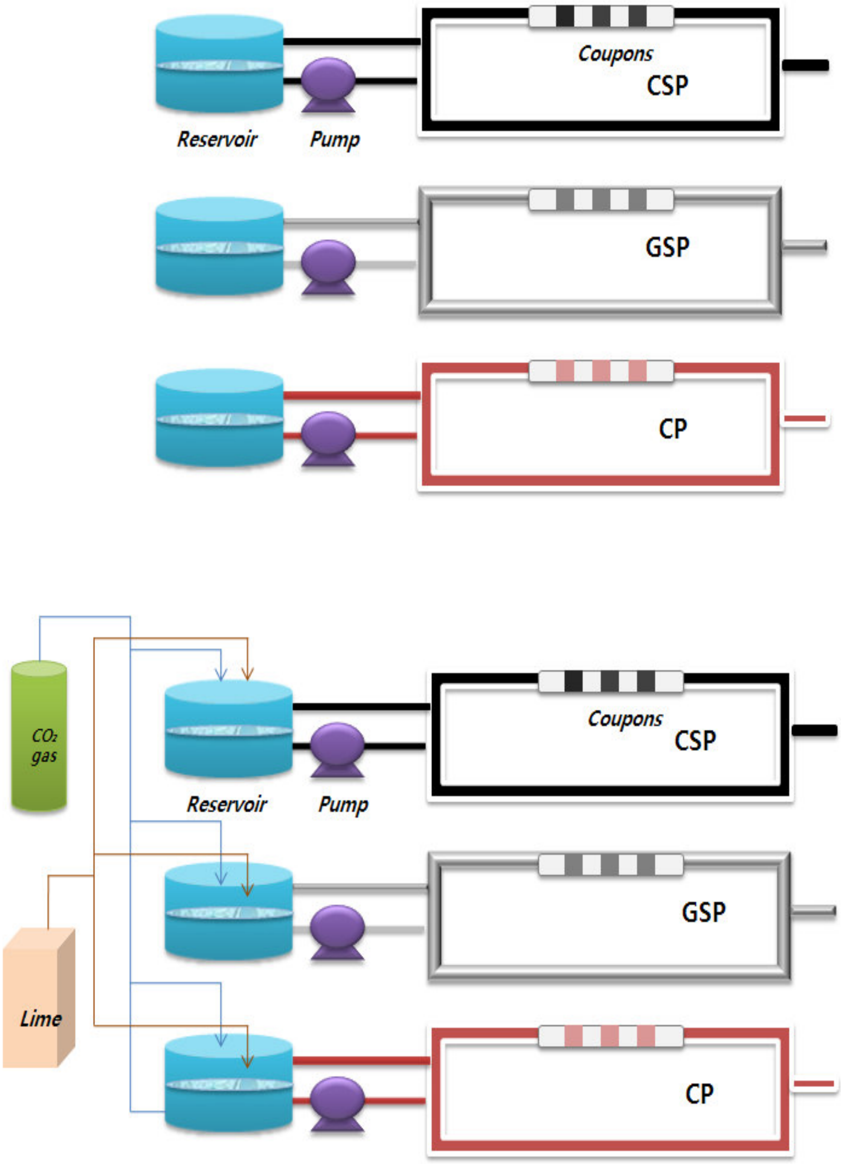


Fig. 1. Schematic diagram of pipe systems (Note : CSP = carbon steel pipe, GSP = galvanized steel pipe, CP = copper pipe)

The condition of pH, alkalinity and calcium ion was regulated to control corrosion control effects on pipe materials in the tap water. Pipe systems consisted of both conditions for the condition of tap water without any treatment and the addition of $Ca(OH)_2$ and CO_2.

The feed water for the pipe systems of $Ca(OH)_2$ and CO_2 was prepared as follows; 50 mg/L of Ca^{2+} was dosed by using $Ca(OH)_2$ and successively, CO_2 gas was injected to create controlled water pH conditions between 7.6 and 7.8.

The samples were used tap water in Konkuk University and the water quality is presented in Table-1. The value of LI and RI was shown to be -1.9 and 10.8, respectively for this tap. These values presented corrosivity in the supplied water. The structure of pipe surface and composition was analyzed by SEM/EDS (energy dispersive spectroscopy).

TABLE-1
CHARACTERISTICS OF TAP WATER QUALITY

Item	Conditions
pH	7.0 ± 0.2
Alkalinity (mg/L as $CaCO_3$)	30 ± 5
Hardness (mg/L as $CaCO_3$)	61 ± 5
Calcium hardness (mg/L as $CaCO_3$)	36 ± 5
Sulfate (mg/L)	20 ± 5
Chloride (mg/L)	20 ± 5
Conductivity (μΩ/cm)	200 ± 20
Water temperature (ºC)	18 ± 5
LI	-1.9
RI	10.8

The analysis of current and potential corrosion status was measured by Autolab PGSTA20 potentiostat/galvanostat with electrochemical software GPES version 4.4. The 300 mL of glass cell for sample analyzing connected with the potentiostat apparatus on the electrode of reference, counter and working. The reference electrode is the Ag/AgCl electrode and the counter electrode is 2 mm of stainless steel. The diameter of the sample holder is 14 ± 1 mm and the water exposed surface area is 0.785 cm^2.

RESULTS AND DISCUSSION

Variation of water quality on chemicals: The variation of pH, alkalinity and the indices of corrosion after addition of NaOH, $Ca(OH)_2$, $NaHCO_3$ and $NaHCO_3$ was evaluated (Fig. 2-5) to select the suitable control chemical for adjusting corrosive water quality. Increasing dosages of those chemicals could make the levels of pH and alkalinity high in the water. The increase of a unit dose for the chemicals, $Ca(OH)_2$ and NaOH easily brought the increase of pH. But, for the case of $NaHCO_3$, the portion of pH that increased was not as great as the additional concentration over 4 mg/L and the pH condition could not be controlled by $NaHCO_3$ over the value of pH 8.

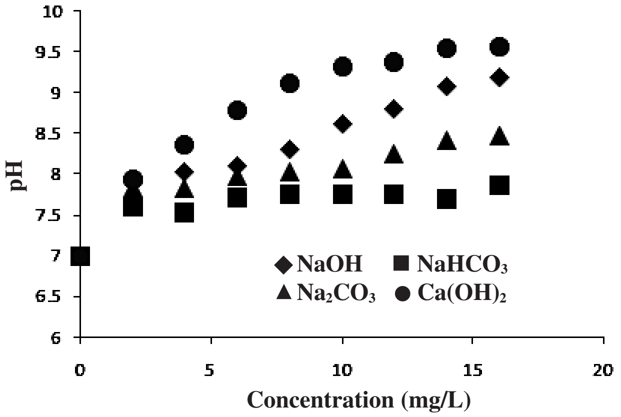


Fig. 2. Variation of pH with NaOH, $NaHCO_3$, Na_2CO_3 and $Ca(OH)_2$

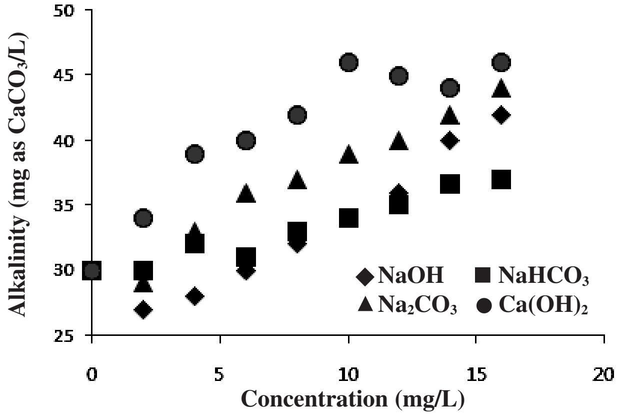


Fig. 3. Variation of alkalinity with NaOH, $NaHCO_3$, Na_2CO_3 and $Ca(OH)_2$

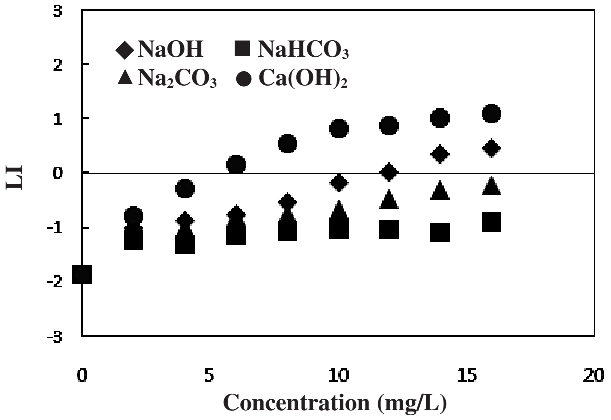


Fig. 4. Variation of LI with NaOH, $NaHCO_3$, Na_2CO_3 and $Ca(OH)_2$

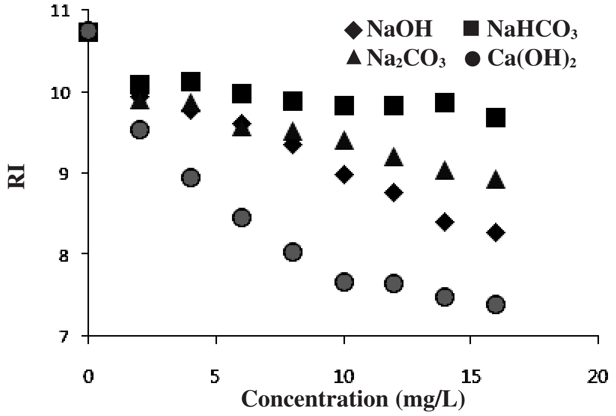


Fig. 5. Variation of RI with NaOH, $NaHCO_3$, Na_2CO_3 and $Ca(OH)_2$

This result indicated the application of $NaHCO_3$ for controlling the pH condition in water might have a problem with excessive doses of chemicals.

The increase of alkalinity was shown to have results similar to that of pH. An alkalinity increase for $NaHCO_3$ was the lowest for the unit dose in the selected agents. In addition, the cost of $NaHCO_3$ was estimated to be higher than others per unit of alkalinity increase by pervious report[13]. And the higher order of alkalinity increase on unit doses of chemicals was shown with $Ca(OH)_2$, Na_2CO_3, NaOH and $NaHCO_3$. The dose of $Ca(OH)_2$ can be expected to contribute the additional benefit of calcium levels in water with the effective increase of pH and alkalinity.

The negative value of LI is regarded as the presentation of corrosiveness in water. The value of the LI index was positive over doses of 6 and 10 mg/L for $Ca(OH)_2$, NaOH, respectively (Fig. 4). Therefore, according to these results, the use of $Ca(OH)_2$ was effective to control corrosive water quality with a low dose. The application of $Ca(OH)_2$ was selected as a chemical for controlling corrosive water quality in rig systems for this experiment.

The value of RI decreases with a dose increase of $Ca(OH)_2$, Na_2CO_3, NaOH and $NaHCO_3$. However, the RI was 9.7 with 16 mg/L of $NaHCO_3$. This result shows the value of RI did not distinctively decrease with a dose of $NaHCO_3$. The level of RI was shown to be over 6.8 with a dose of 16 mg/L, the highest tested dose, for all tested chemicals in this experiment (the level of RI between 6.8 and 8.5 represents corrosive characters for water). In four tested chemicals, $Ca(OH)_2$ showed the highest decrease of RI on chemical dose.

Effect of corrosion control on pipe materials: The level of metal release and corrosion velocity by using coupons weight differences were monitored in carbon steel, galvanized, copper pipes. The level of Fe with application of $Ca(OH)_2$ and CO_2 was compared with the tap water condition without any treatment.

The detected concentration of Fe was relatively high at the initial operation time owing to impurities attached on the pipe surface and cut pipe particles during piping system manufacturing (Fig. 6). For the carbon steel pipe, the Fe concentration released did not exhibit a big difference between the control and the $Ca(OH)_2$ and CO_2 treated tap water before 30 d of operation. The level of Fe decreased in the carbon steel pipe during the treatment of $Ca(OH)_2$ and CO_2 on contact time. The effective formation of protective films on pipes was reported at the controlled condition of 60 mg $CaCO_3$/L, LI 0.3 by applying with $Ca(OH)_2$ and CO_2[19].

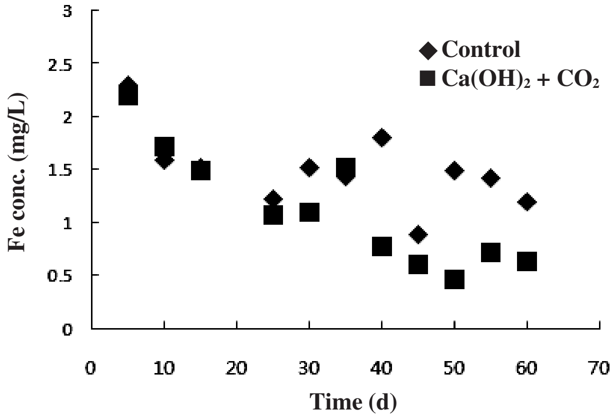


Fig. 6. Comparison of Fe concentration released between the non-treated tap water and $Ca(OH)_2$ and CO_2 treated tap water in carbon steel pipes

The study at Portland, Oregon showed Zn and Fe were the main corrosion by-product in taps joined to galvanized pipes. The mean level of Zn and Fe was 0.5 and 1.1 mg/L at Portland[20]. The release level of Zn is presented in Fig. 7 in galvanized iron pipes during the set operation time. Zn content release is often presented after installation of the new pipe system[13]. The mean concentration of Zn was 1.13 mg/L for the condition without application of $Ca(OH)_2$ and CO_2, a value over the Korean standard of drinking water (1 mg/L). The use of galvanize pipes is currently prohibited in Korea for the plumbing and distribution of drinking water. However, the thorough management for already laid pipe lines is required to correspond with the concern of zinc release. The concentration of Zn decreased as operation time progressed. The level of Zn at 5 d of operation time was 1.7 and 2.3

times higher than that at 60 d without any treatment and pipe systems treated with $Ca(OH)_2$ and CO_2, respectively. Zn levels in water without any treatment were shown to be 1.7 times higher than that for the water treated with $Ca(OH)_2$ and CO_2 at 60 d of operation.

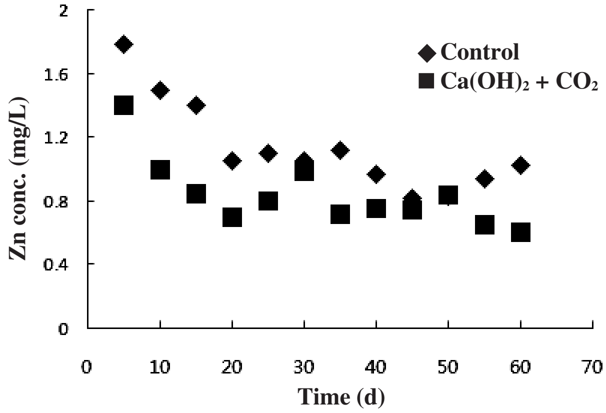


Fig. 7. Comparison of Zn concentration released between the non-treated tap water and $Ca(OH)_2$ and CO_2 treated tap water in galvanized iron pipes

The level of Fe for the galvanized iron pipes is presented in Fig. 8. The difference of Fe concentration between conditions treated with $Ca(OH)_2$ and CO_2 and non-treatment conditions was not great. The concentration of Fe decreased over time. The Fe content at 5 d of operation was 2.2 and 2.5 times higher than that at 60 d for the pipe system without any treatment and treated pipe system with $Ca(OH)_2$ and CO_2, respectively. At 60 d, the concentration of Fe was 0.25 and 0.20 mg/L for the tap water treated with $Ca(OH)_2$ and CO_2 and tap water without any treatment, respectively.

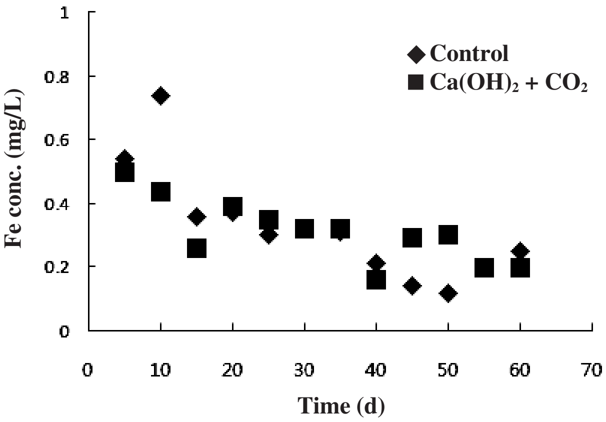


Fig. 8. Comparison of Fe concentration released between the non-treated tap water and $Ca(OH)_2$ and CO_2 treated tap water in galvanized iron pipes

The level of Cu decreased after treatment of $Ca(OH)_2$ and CO_2 in copper pipe (Fig. 9). The copper concentration decreased with operation time. The copper concentration ratio for the treated condition of $Ca(OH)_2$ and CO_2 at 60 d compared to 5 d was 0.4. Ryder and Hoyt[21] reported 25 % of corrosion velocity decreased after 1 month of operation with the simultaneous treatment of the zinc orthophosphates and that the $Ca(OH)_2$ and the pH control method was more effective than using higher concentrations of corrosion inhibitors.

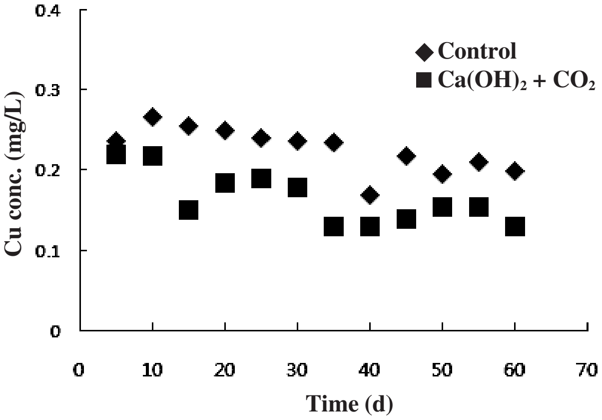


Fig. 9. Comparison of Cu concentration released between the non-treated tap water and $Ca(OH)_2$ and CO_2 treated tap water in copper pipes

The corrosion velocity for carbon steel pipe is presented in Fig. 10 for conditions of non-treatment and treatment with $Ca(OH)_2$ and CO_2 on operation time. The corrosion velocity at 5 d was 5.6×10^{-2}, 5.6×10^{-3}, 8.5×10^{-4} mm/year for carbon steel pipe, galvanized pipe, copper pipe in the non-addition condition. The corrosion velocities for carbon steel pipe was shown to be 10 and 66 times that of galvanize and copper pipe. However, variations of corrosion velocity for the treatment of $Ca(OH)_2$ and CO_2 was constant without a great change after 40 d of operation time. At 60 d, the corrosion velocity for the tap water without any treatment and that of water treated with $Ca(OH)_2$ and CO_2 was 4.26×10^{-2}, 3.75×10^{-2} mm/year, respectively.

The effect of corrosion control was evident for the galvanized iron pipe compared to carbon steel pipe with the application of $Ca(OH)_2$ and CO_2 (Fig. 11). The mean corrosion velocity during 60 d of operation time for tap water without any treatment was shown to be 2.2 times higher than that of the water treated with $Ca(OH)_2$ and CO_2. The corrosion velocity for tap water conditions without treatment was 3.6 times higher than $Ca(OH)_2$

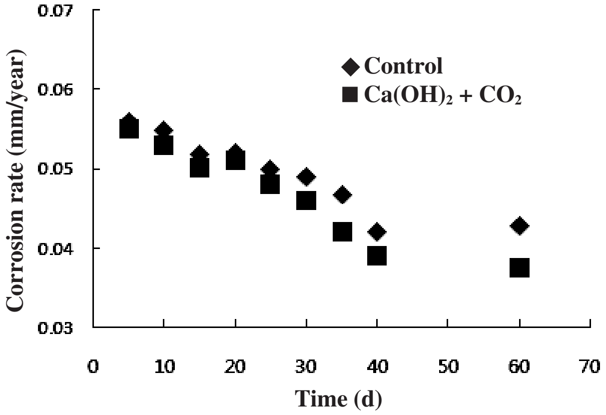


Fig. 10. Corrosion rate for the non-treated tap water and $Ca(OH)_2$ and CO_2 treated tap water in carbon steel pipe

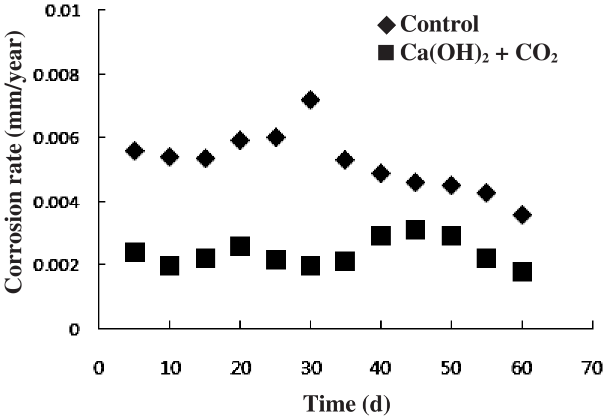


Fig. 11. Corrosion rate for the non-treated tap water and $Ca(OH)_2$ and CO_2 treated tap water in galvanized iron pipe

and CO_2 treated water at the time of 30 d. The corrosion velocity for tap water increased till 30 d and then decreased after that time. But the curve for corrosion velocity was comparatively stable without any great change for the treated condition of $Ca(OH)_2$ and CO_2 during the entire operation time. Bächle *et al.*[22] demonstrated the corrosion rate of Zn was correlated with the pH condition of galvanized pipe. They observed that the corrosion rate increased with decreasing pH between pH 7 and 8 in galvanized pipe.

The corrosion velocity in copper pipe was compared in Fig. 12 between tap water without any treatment and those treated with $Ca(OH)_2$ and CO_2. The corrosion velocity for the copper increased within narrow

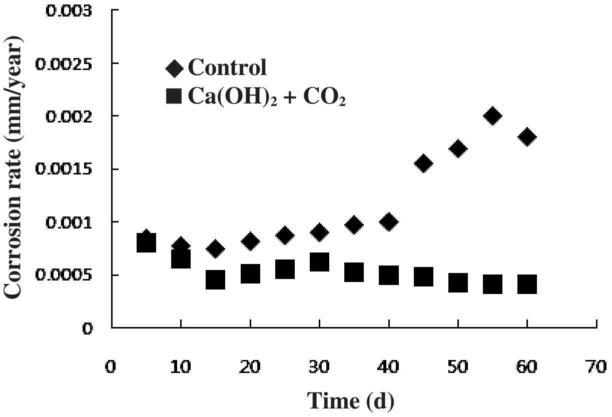
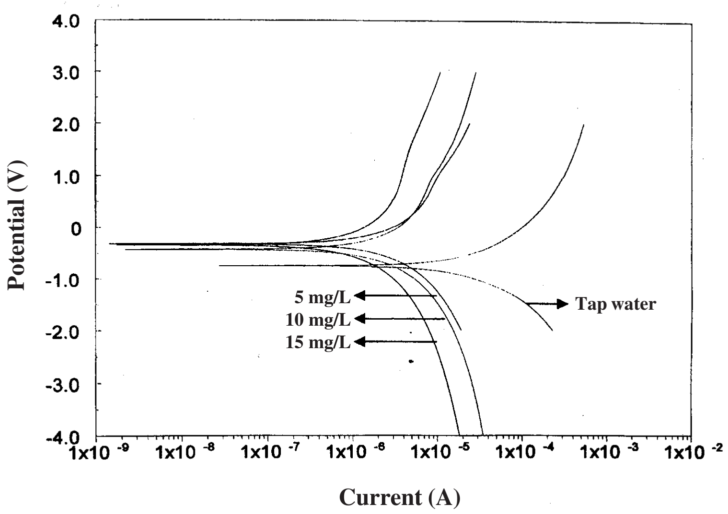


Fig. 12. Corrosion rate for the non-treated tap water and $Ca(OH)_2$ and CO_2 treated tap water in copper pipe

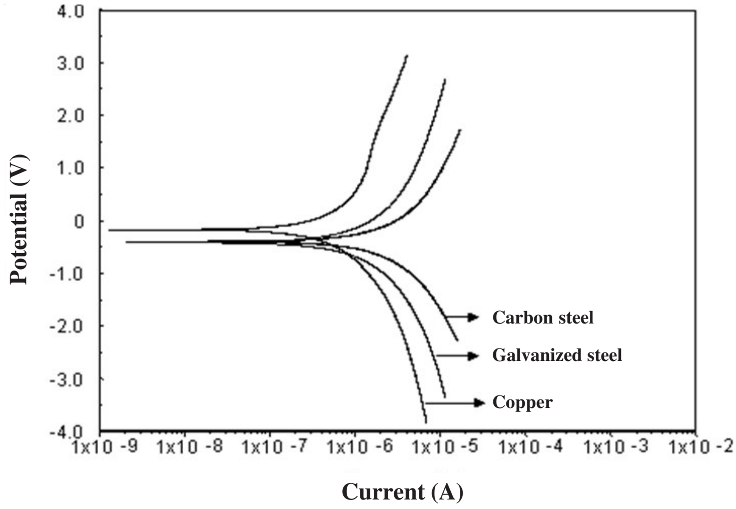
limits before 40 d and then it increased rapidly afterwards. The highest value was shown at the 55 d of operation time. While, the corrosion velocity was constant during 60 d operation for the $Ca(OH)_2$ and CO_2 treated pipes system. The corrosion velocity was no different at the initial operation period between both the conditions, the differences of corrosion velocity increased with operation time. The corrosion velocity for the non-treatment systems was 4.4 times higher than that of the $Ca(OH)_2$ and CO_2 treated pipes system at 60 d of operation time.

The corrosion current and potential for carbon steel, galvanized iron and copper pipe coupons with $Ca(OH)_2$ addition and comparisons between non-addition conditions and addition conditions with $Ca(OH)_2$ levels of 5, 10 and 15 mg/L are presented in Fig. 13. The corrosion current density decreased with addition levels of $Ca(OH)_2$. The higher order of corrosion rate was shown in carbon steel, galvanized iron and copper pipes. These results have appeared to exhibit the same tendency as those of corrosion velocity using coupon weight differences.

Observation of metal surface and scale substances: The analysis result of scale substances formed on carbon steel and galvanized pipe is presented in Table-2. The scale layer appeared as a reddish black colour on carbon steel pipes. For the contact with tap water, the main substance was Fe, which it holds 96.4 %. Calcium occupied 0.74 %. The substance of Fe decreased and Ca increased after additional treatment of $Ca(OH)_2$ and CO_2. Si which is an element of sand and soil, was shown in a distribution of 2.84 and 2.19 % for the condition of non-addition and addition of $Ca(OH)_2$ and CO_2, respectively.



(a) Application effect of Ca(OH)$_2$



(b) Influence on different pipe materials

Fig. 13. Tafel polarization curves

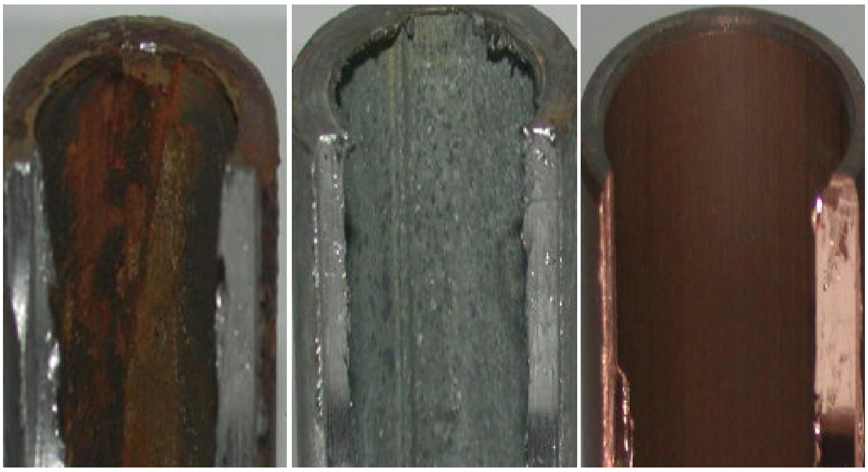
The distribution of Zn was 87.8 %, which was the main plating substance on galvanized iron pipe and those of Fe and Al were 2.39, 1.01 % for the case of contact with tap water. The ratio of Zn was also ranked highest for the treated condition of Ca(OH)$_2$ and CO$_2$. The substances of Fe and Al were distributed 2.41 and 2.26 % with the treated condition of Ca(OH)$_2$ and CO$_2$. The substance distribution of Ca was 1.09 % for the treatment

TABLE-2
EDS ANALYSIS OF SCALE SUBSTANCES ON PIPES

	Carbon steel pipe	Galvanized iron pipe
Control (tap water)	Si 2.84 % Ca 0.74 % Fe 96.41 %	Si 8.78 % Fe 2.39 % Zn 87.82 % Al 1.01 %
Treatment of $Ca(OH)_2$ and CO_2	Si 2.19 % Ca 1.90 % Fe 95.91 %	Al 2.26 % Si 5.08 % Fe 2.41 % Zn 89.16 % Ca 1.09 %

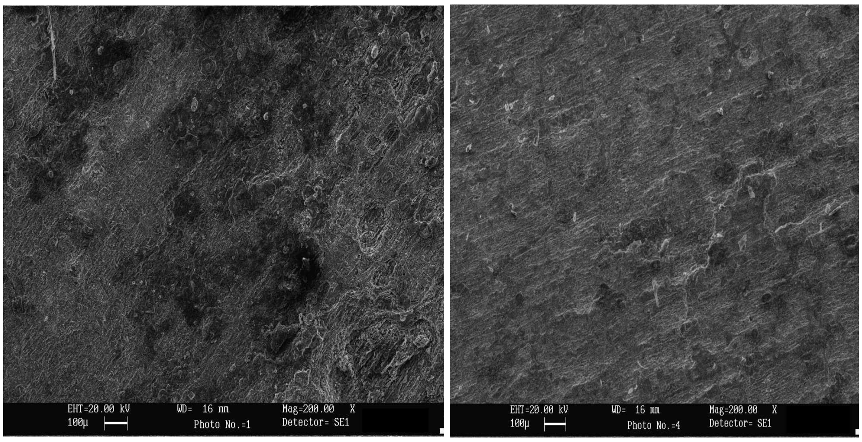
of $Ca(OH)_2$ and CO_2. Lee *et al.*[10] reported $CaCO_3$ and Fe_3O_4 were detected in the analysis of the cast iron coupon. The amount of formed scale on copper pipe was not enough to analyze by energy dispersive spectroscopy (EDS), so we could not present the data of scale substances on copper pipe.

The inside of the pipe surface was observed by SEM for carbon steel and galvanized iron pipes. Unsmoothed metal surfaces were observed for the non-treatment condition by corrosive tap water (Fig. 14). The release fragments of zinc galvanizing were seen on galvanized iron pipes with the contact with tap water during 60 d of operation (Fig. 15). A less damaged surface of metal was observed for the addition condition of $Ca(OH)_2$ and CO_2. It might contribute to the formation of protective films with the dose of $Ca(OH)_2$ and CO_2.



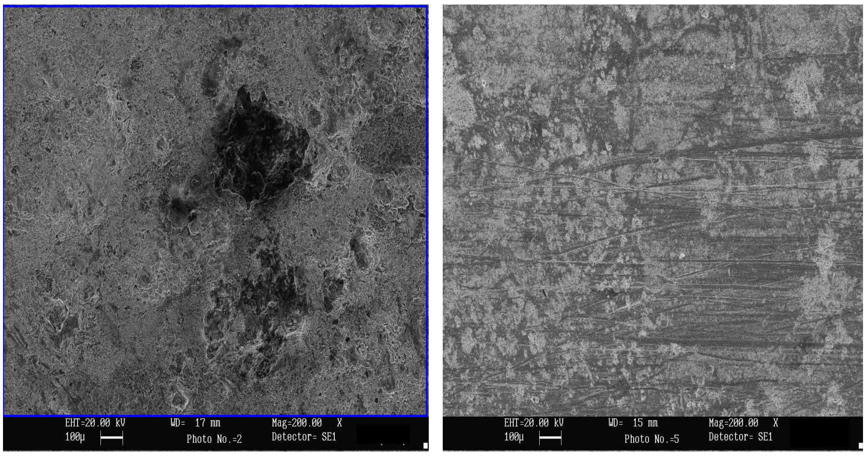
(a) Carbon steel pipe (b) Galvanized pipe (c) Copper pipe

Fig. 14. Photographs of carbon steel, galvanized and copper pipe for the tap water without any treatment



(a) Carbon steel without any treatment

(b) Carbon steel for the treatment of $Ca(OH)_2$ and CO_2



(c) Galvanized steel without any treatment

(d) Galvanized steel for the treatment of $Ca(OH)_2$ and CO_2

Fig. 15. SEM photos of carbon steel and galvanized pipe

Conclusion

This research was carried out to select suitable alkalinity agent for corrosion control in water distribution systems and to evaluate the effect of corrosive water quality controlling. The experiment was performed with the tap water which has corrosive water quality in plumbing systems installed at a laboratory in the engineering building of Konkuk University. The supplied water was compared with non-treated conditions and conditions treated with $Ca(OH)_2$ and CO_2. The corrosion control effect was compared for the different pipe materials such as carbon steel, galvanized iron and copper pipe.

(1) NaOH, Na_2CO_3, $NaHCO_3$ and $Ca(OH)_2$ were compared for controlling efficiency of corrosive water quality to select a suitable agent. The use of $Ca(OH)_2$ easily attained an increase in pH and alkalinity with a unit dose level of $Ca(OH)_2$. The water corrosivity control by the evaluation of LI was effectively attained. (2) The release levels of metals were decreased after treatment of $Ca(OH)_2$ and CO_2. The mean value of Fe, Zn and Cu in non treatment pipe appeared to be 1.3, 1.4 and 1.4 times higher than those treated with $Ca(OH)_2$ and CO_2 for carbon steel, galvanized and copper pipe, respectively. Therefore, the application of $Ca(OH)_2$ would be useful to control corrosion and metal release in water pipe systems. (3) The decrease of corrosion current was observed with the application of $Ca(OH)_2$. The higher order of corrosion rate ranked to carbon steel, galvanized iron and copper pipe on pipe materials. The main scale substances on carbon steel, galvanized pipe were Fe and Zn and amounts were 95.9 and 89.2 %, respectively. The ratio of Ca in scale on pipes increased with the application of $Ca(OH)_2$ compared to controlled tap water.

REFERENCES

1. T.H. Kim, Y.J. Lee. H. Lee, C.H. Lee, K.C. Ann and W.S. Lee, *J. Environ. Sci.*, **16**, 121 (2007).
2. P.J. Kwak, S.I. Kim, D.S. Woo and S.H. Nam, *J. Korean Soc. Water Wastewater*, **13**, 134 (1999).
3. Y.B. Park and S.H. Kong, *J. Korean Ind. Eng. Chem.*, **16**, 372 (2005).
4. P.J. Kwak, H.D. Lee, S.H. Nam and W.S. Chung, *J. Korean Soc. Environ. Eng.*, **23**, 1195 (2001).
5. K.H. Jo, S.I. Kim and D.S. Woo, *J. Environ. Health*, **33**, 43 (2007).
6. International Standards Organization, Manual of Symbols and Terminology for Physicochemical Quantities and Units: 2nd revision, p. 141 (1979)
7. M.G. Fontana and N.D. Greene, Corrosion Engineering: Korean Student Edition, McGraw-Hill Book Company, p. 28 (1984).
8. KICT and KOWACO, Development of Prediction Model of Aging and Corrosion Status on Distribution System: 1st report (2000).
9. H.C. Lee, H. Lee, C.G. Jung and Y.J. Lee, *Korean J. Environ. Health*, **29**, 1 (2003).
10. J.I. Lee, J.K. Lim, S.H. Seo, D.Y. Kim and C.H. Shin, *J. Environ. Sci.*, **9**, 505 (2000).
11. G.H. Seo, H.D. Lee, W.S. Chung and C.S. Gee, *J. Korean Soc. Environ. Eng.*, **20**, 1151 (1998).
12. Y.J. Lee and S.H. Nam, *Korean J. Environ. Health*, **29**, 65 (2003).
13. AWWA Research Foundation, Internal Corrosion of Water Distribution System, edn. 2 (1996).
14. C. Volk, E. Dundore, J. Schiermann and M. LeChevallier, *Wat. Res.*, **34**, 1967 (2000).
15. P. Boissonneault, AWWA WQTC Proc., p. 1693 (1994).
16. G.K. Elmund, B. Alexander and K. Gertig, AWWA WQTC Proc., p. 681 (1992).
17. I. Wagner, Proc. EUROCORR European Congress on Metallic Corrosion (1977).
18. D.T. Morrill and R.L. Sank, *J. AWWA*, **69**, 592 (1977).
19. L. Legrand and P. Leory, Prevension of Corrosion and Scaling in Water Supply Systems, Ellis Harwood (1990).
20. J.M. Montgomery Consulting Engineers, International Corrosion Mitigation Study, Final Report (1982).
21. R.A. Ryder and B.P. Hoyt, AWWA Annual Conference (1977).
22. A. Bächle, E. Deschner, H. Weiss and I. Wagner, *Werkstoffe und Korrosion*, **32**, 435 (1981).

(*Received*: 25 March 2008; *Accepted*: 30 May 2008) AJC-6603