Practical Paper

Development and implementation of a corrosion control algorithm based on calcium carbonate precipitation potential (CCPP) in a drinking water distribution system

Do-Hwan Kim, Dong-Youn Kim, Soon-Heon Hong, Ji-Won Kim
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ABSTRACT

Water corrosiveness depends mainly on the chemical factors of pH, alkalinity, Ca^{2+} concentration, dissolved oxygen, and total dissolved solids (TDS), and on the physical factors of temperature and flow velocity as well as pipe materials. The calcium carbonate precipitation potential (CCPP) control process and a simulated water distribution system (SWDS) were installed for a pilot-scale advanced water treatment process. The system was operated for 2 years. The CCPP control algorithm for anti-corrosion of a pipeline was developed and validated. The target CCPP value could be controlled by manipulating the pH and alkalinity with additions of sodium carbonate (Na_2CO_3) and carbon dioxide (CO_2) where enough calcium was present. The CCPP range of $0 \sim 4\,mg\,L^{-1}$ was controlled reasonably to induce a calcium carbonate ($CaCO_3$) film on the surface of the pipeline, which provided the anti-corrosion effect. The proper range required of pH and alkalinity used to manipulate the range of $0 \sim 4\,mg\,L^{-1}$ of CCPP was $8.0 \sim 8.3$, $70 \sim 100\,mg\,L^{-1}$ as $CaCO_3$ when the Ca^{2+} concentration was in the range of $60 \sim 80\,mg\,L^{-1}$ as $CaCO_3$, respectively, in this research. The effect of corrosion control was demonstrated by reduced iron and zinc concentrations released from the pipe material. This result might indicate the presence of the $CaCO_3$ film and the efficacy of its anti-corrosion effect. However, the simple proportional integral derivative (PID) controller's sensitivity seemed to be in need of further improvement.

Key words | $CaCO_3$, CCPP, corrosion control, corrosiveness, water distribution system

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INTRODUCTION

The corrosion of pipelines in water distribution systems is caused by electrochemical reactions occurring from contact between the metal pipe surface and water. It is affected by the water corrosiveness as well as pipe materials. Water corrosiveness depends mainly on the chemical factors of water such as pH, alkalinity, dissolved oxygen, and total dissolved solids (TDS), and on the physical factors such as temperature and flow velocity. The pipe material is also an important factor when considering potential corrosion phenomena in water

distribution systems. In the water treatment process, pH, alkalinity, and calcium concentrations are usually manipulated for color removal and corrosion control. This can also prevent internal corrosion of a water distribution system (Michael & Susan 1982; AWWARF 1996; Volk *et al.* 2000; Rooklidge & Ketchum 2002).

The corrosiveness of tap water can be estimated by corrosion indexes, which are used to predict potential corrosion and to provide information on the corrosiveness

of water. The representative corrosion indexes are based on calcium carbonate precipitation measures such as the Langelier Saturation Index (LSI), the Larson Index (LI), the Ryznar Index (RI), and the Calcium Carbonate Precipitation Potential (CCPP) (AWWARF 1996). Saturation indices such as Langelier's index have been applied to anti-corrosion techniques for copper or galvanized pipes. However, a saturation index is not a suitable predictor of the anti-corrosion capabilities of stainless steel or other materials (Berghult *et al.* 2001). The LSI provides a relative assessment of the saturation state of water. However, this assessment is qualitative only, in that it does not quantify the actual amount of mineral that will precipitate if the water attains saturation equilibrium (Loewenthal *et al.* 2004). The CCPP is a more reliable water stability index to use since this index provides a quantitative measure of the calcium carbonate deficit or excess of the water, giving a more accurate guide as to the likely extent of $CaCO_3$ precipitation (Sarin *et al.* 2004).

When the water has high hardness, the CCPP can be used as an anti-corrosion index. This index can be used for inducing an over-saturated calcium concentration by only increasing pH. The CCPP can be calculated with pH, alkalinity, calcium concentration, total dissolved solids (TDS), and temperature, or determined by RTW (Rothberg, Tamburini & Winsor) model (RTW Inc. 1996). Over-saturated Ca^{2+} is precipitated as a form of $CaCO_3$ on the surface of a pipe and can help to prevent pipe corrosion by preventing contact between the pipe surface and the water. When the water is soft, the calcium hydroxide ($Ca(OH)_2$) can be added to increase the calcium concentration and create the proper condition for $CaCO_3$ precipitation. Carbon dioxide (CO_2), sodium hydroxide (NaOH), and sodium carbonate (Na_2CO_3) can also be injected to induce proper pH and alkalinity levels to form a $CaCO_3$ film on the surface of the pipe. The CCPP of calcium-oversaturated water was reported to be in the range of $4 \sim 10 \, mg \, L^{-1}$ of $CaCO_3$ for corrosion protection of pipe (Merrill & Sanks 1977; Benefield *et al.* 1982), where the resulted pH was over 8.5. In Korea the pH standard for drinking water is $6.5 \sim 8.5$. Therefore the CCPP should be lower than $4 \, mg \, L^{-1}$ of $CaCO_3$.

The purpose of this paper was to develop and validate the CCPP control algorithm for anti-corrosion of pipelines by manipulating pH and alkalinity. Also, the possibility of anti-corrosion capabilities was confirmed at a low level of below $4 \, mg \, L^{-1}$ of CCPP. Proper ranges of pH and alkalinity were tested for various Ca^{2+} concentration ranges of CCPP.

MATERIALS AND METHODS

Set-up for pilot scale experiments

An advanced water treatment pilot plant was located at the Institute for Water Quality Research, Busan Metropolitan City, Korea. The plant consisted of various treatment stages which included, pre-ozonation, coagulation, sedimentation, sand filtration, post-ozonation, and biological activated carbon (BAC) adsorption. Its capacity was $80 \, m^3 day^{-1}$.

Then the simulated water distribution system (SWDS) was connected to the above water treatment plant as shown Figure 1. The control system for the corrosiveness of water was installed into the plant using a PID controller. The materials of the SWDS consisted of steel, ductile cast iron pipe, galvanized steel, stainless steel, and copper. Their specifications are shown in Table 1. However, for evaluating the effectiveness of the corrosion control only the water samples from the galvanized steel pipes were collected for this work. The experiment was conducted continuously for 12 months, from November 2002 to December 2003.

Since the effluents from the water treatment plant were input to the SWDS, their measured and target water quality data were summarized in Table 2. For controlling the anti-corrosion the pH and alkalinity of the influent of the control tank were manipulated by the addition of Na_2CO_3 and CO_2. Its control scheme is explained in detail in the following section. The adjusted water was introduced into the SWDS. In order to monitor the input into the SWDS the on-line sensors for pH, temperature, and TDS and the automatic measuring instruments for alkalinity and calcium hardness were used for collecting data in the influent and effluent areas of the control tank. At the end of the SWDS the water samples were collected manually and the iron and zinc were measured with ICP/MS (ICP JOBIN YVON 50P) which are used for evaluating the effect of the anti-corrosion control. The CCPP was calculated using the RTW (Rothberg, Tamburini & Winsor) model ver. 3.0 (RTW Inc. 1996).
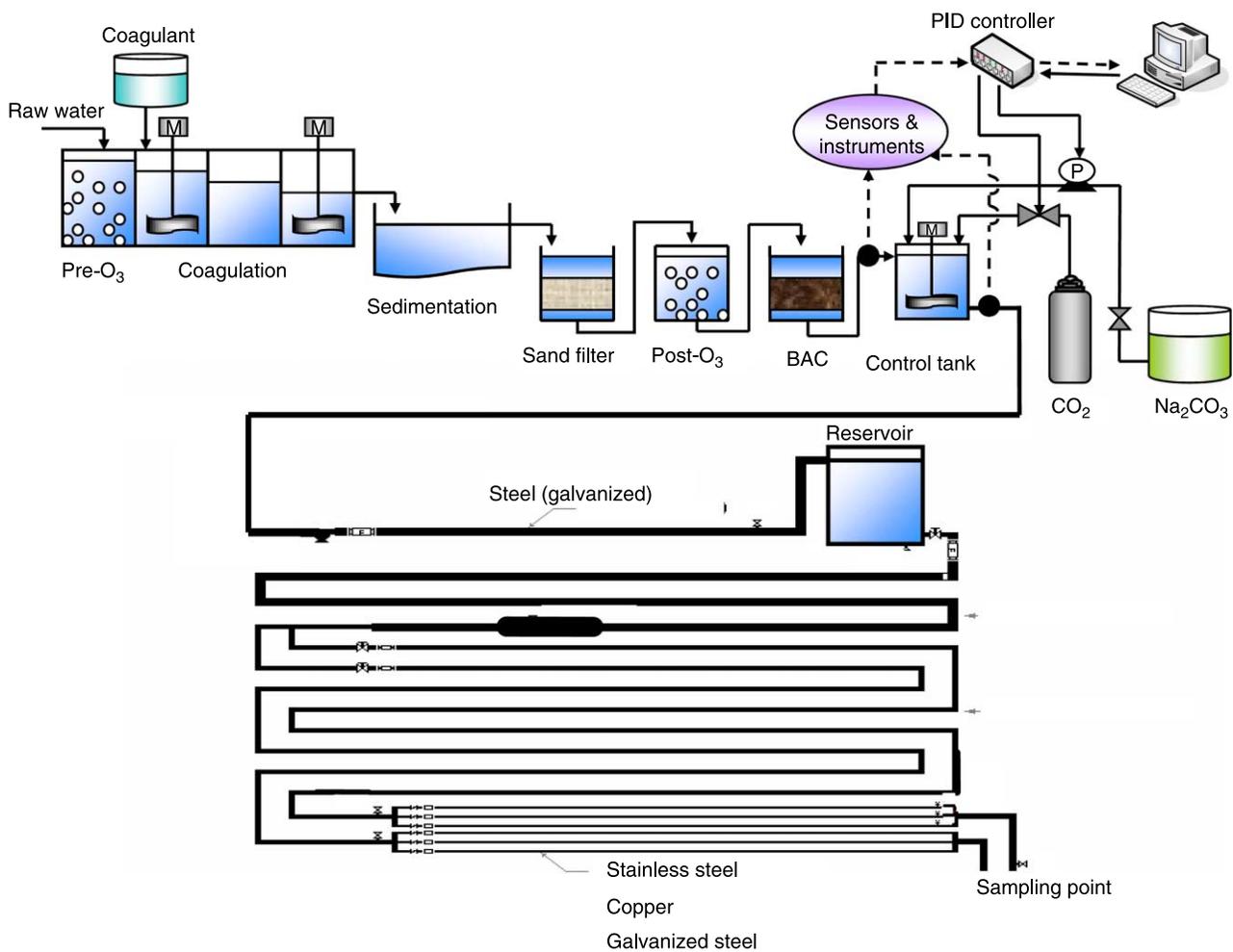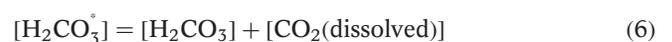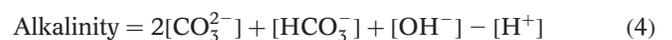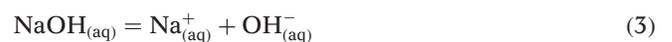
Figure 1 │ Advanced water treatment plant and simulated water distribution system (SWDS) where the corrosiveness of water was controlled based on CCPP.

Development of control algorithm

The control algorithm was developed in principle based on a pC (= −log [species]) vs pH diagram in a carbonic acid system (Benefield *et al.* 1982). The Na_2CO_3 added into the water increases the total alkalinity by introducing a bicarbonate ion (HCO_3^-), carbonate ion (CO_3^{2-}), and

Table 1 │ The composition of the simulated water distribution system (SWDS)

Materials	Diameter (mm)	Length (m)	Velocity (ms^{-1})
Steel	80	141.7	2.5 ~ 2.6
Stainless steel	15	9.0	0.5 ~ 0.8
Copper	15	9.0	0.5 ~ 0.8
Galvanized steel	15	9.0	0.5 ~ 0.8

hydroxyl ion (OH^-) in Equations (1), (2), and (3). At the same time the pH is increased by the reaction on an OH^- ion in Equation (3). For example, $1\,mg\,L^{-1}$ of Na_2CO_3 increases the alkalinity by $0.94\,mg\,L^{-1}$ as $CaCO_3$.

$$Na_2CO_{3(s)} + H_2O_{(1)} = NaHCO_{3(aq)} + NaOH_{(aq)} \tag{1}$$

$$NaHCO_{3(aq)} = Na^+_{(aq)} + HCO^-_{3(aq)} \tag{2}$$

$$NaOH_{(aq)} = Na^+_{(aq)} + OH^-_{(aq)} \tag{3}$$

$$Alkalinity = 2[CO_3^{2-}] + [HCO_3^-] + [OH^-] - [H^+] \tag{4}$$

$$C_T = [H_2CO_3^*] + [HCO_3^-] + [CO_3^{2-}] \tag{5}$$

$$[H_2CO_3^*] = [H_2CO_3] + [CO_2(dissolved)] \tag{6}$$

Table 2 │ pH, temperature, calcium hardness, and alkalinity measured at the SWDS input and their target values for controlling corrosiveness of water

SWDS input	pH	Temp. (°C)	Calcium hardness (mg $CaCO_3L^{-1}$)	Alkalinity (mg $CaCO_3L^{-1}$)
Measured values	5.80 ∼ 7.79 (avg. 6.83)	2.10 ∼ 27.4 (avg. 14.0)	32.8 ∼ 90.9 (avg. 60.1)	14.3 ∼ 61.0 (avg. 37.6)
Target values	8.3	–	–	70, 80, 90, 100

At the pC vs pH diagram in the range of pH 6.3 and 10.3, the HCO_3^- is the main species of the total carbonate species concentration (C_T) and then the alkalinity can be determined based on $[HCO_3^-]$ as the same concentration of C_T and alkalinity (Loewenthal & Marais 1976; Musvoto *et al.* 2000).

If the pH is increased higher than the target pH by producing OH^- from Equation (3), then CO_2 can be added to decrease the pH to the target value. It can be considered that the pH of most natural water is controlled according to the carbonic acid system. When the CO_2 is added into the water the applicable equilibrium reactions follow:

$$CO_{2(g)} + H_2O_{(1)} = (H_2CO_3)_{(aq)} = H^+_{(aq)} + HCO^-_{3(aq)} \qquad (7)$$
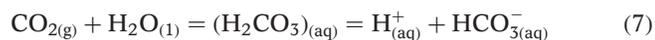
As the H^+ ion is produced by adding CO_2, the C_T is increased by the reaction of $[HCO_3^-]$ and $[CO_3^{2-}]$ and the $[OH^-]$ increased by Equation (3) is reduced by adding $[H^+]$ in the above of Equation (7) to the target pH.

The reason why Na_2CO_3 and CO_2 were selected for controlling the alkalinity and pH, respectively, was because of the following: since the $Ca(OH)_2$ has a very low solubility, the addition of $Ca(OH)_2$ would increase the turbidity at the near end of the treatment system. Furthermore, one has to use a substantial amount to obtain a reasonable result. This is not a favorable condition for the treated water and therefore the Na_2CO_3 and CO_2 were selected rather than $Ca(OH)_2$.

Development of controller

The control algorithm is shown in Figure 2. The control objective was to prevent the corrosion of the pipeline in a water distribution system by maintaining the CCPP in the range of 0 ∼ 4 mg L^{-1} at the input to the SWDS. Since the average calcium concentration in the input to the SWDS was 60.1 mg L^{-1} as $CaCO_3$, its manipulation was not considered in this work. The TDS and temperature were difficult to manipulate. Among these, the pH and alkalinity

were the most influential factors. Therefore, even though the CCPP was a control variable, the alkalinity and pH were used as the manipulated variables. To increase the alkalinity to a certain manipulating value the Na_2CO_3 was injected. The alkalinity was calculated according to the procedures found in the reference (Benefield *et al.* 1982). The required Na_2CO_3 was calculated by following equation:

$$Na_2CO_3 \text{ required}[moleL^{-1}] = [Alk.]_{desired} - [Alk.]_{initial}$$
$$= \Delta[Alk.] \qquad (8)$$

where

$[Alk.]_{desired}$ target concentration of alkalinity

$[Alk.]_{initial}$ concentration of alkalinity before Na_2CO_3 added to water

$\Delta[Alk.]$ variation of alkalinity concentration

By doing this the pH was increased together with alkalinity. To decrease the pH lower than or near 8.3, CO_2 gas was injected. The target pH of 8.3 was set due to the drinking water regulation. The required CO_2 gas amount was calculated in the following equation:

$$CO_2 \text{ gas required }[moleL^{-1}] = [C_T]_{desired} - [C_T]_{initial}$$
$$= \Delta[C_T] \qquad (9)$$

where

$[C_T]_{desired}$ target concentration of C_T after CO_2 added to water

$[C_T]_{initial}$ C_T concentration after Na_2CO_3 added to water

$\Delta[C_T]$ variation of concentration according to C_T by CO_2

This control action was implemented every 5 minutes. However, in practice, the variation of pH is affected not only by added Na_2CO_3 and CO_2 but also by the buffer intensity of the water. The buffer intensity is defined as the number of moles of strong acid or strong base required to
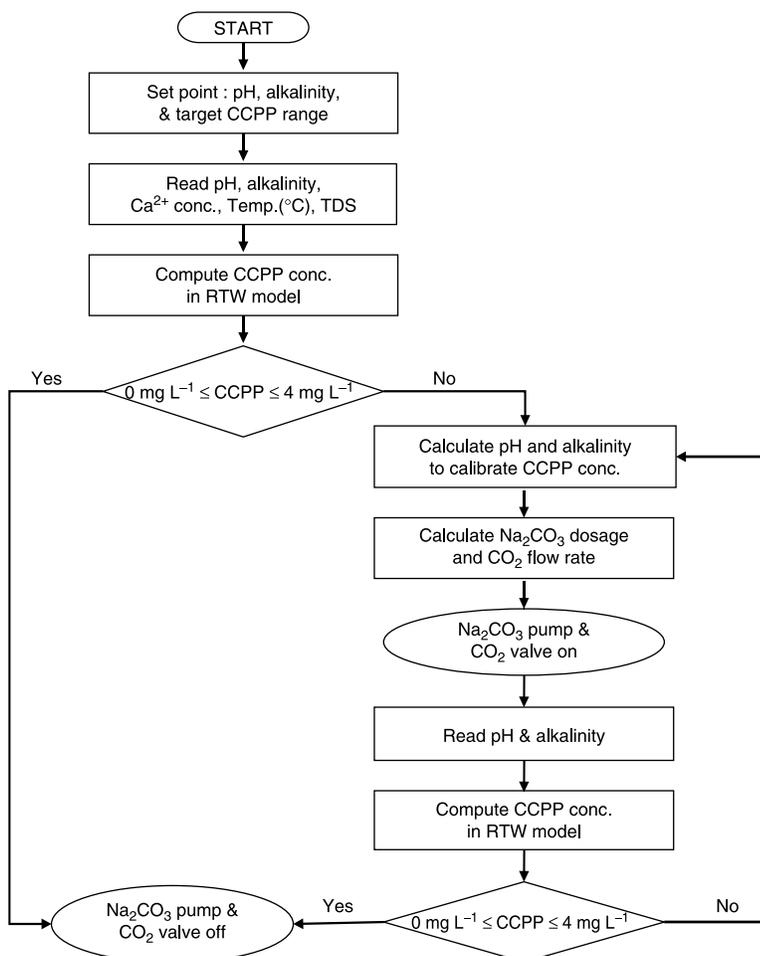
Figure 2 | Flow sheet of control algorithm for control CCPP by manipulating alkalinity and pH to reduce corrosiveness of water.

change the pH of 1 litre of solution by one pH unit. Natural water usually has strong buffer intensities. Alkalinity, pH, and buffer intensity are all interrelated, and changing one of these will also change the others. In addition to the high buffer intensity at extreme pH values, there are two regions of maximum buffer intensity close to pH values of 6.3 and 10.3 at constant temperature (25°C) on the pC-pH diagram for carbonate system (Weber & Stumm 1963; Snoeyink & Jenkins 1980; Zhang 2000; McNeill & Edwards 2001). Therefore, the amount of added Na_2CO_3 and CO_2 cannot result in the proportional variation of pH. These phenomena make it very difficult to manipulate the pH control.

To overcome this difficulty the range between desired and initial values were divided into 100 increments and the Na_2CO_3 and CO_2 dosages were determined by calculating at each fraction of incremental changes according to buffer intensity changed of pC line by pH variation and then summing them up. The equation for calculating the proper Na_2CO_3 and CO_2 dosages of Equations (8) and (9), considering the buffer intensity.

Verification of the controller by bench-scale experiment

To verify the developed control algorithm and controller, it was tested by the bench-scale experiment as a batch mode. Because the alkalinity and pH of the SWDS input are low, they should be increased to create an over-saturated condition of $CaCO_3$. For our bench-scale experiment, the SWDS input was sampled in a 1 L cap-bottle and the pH

and alkalinity of the sample were measured. The target pH was determined to be 8.3 and the alkalinity set-points were 70, 80, 90, and 100 mg L^{-1} as CaCO$_3$. The dosage of 0.1 N Na$_2$CO$_3$ and volume of 99.9% CO$_2$ were calculated for 1 L of the SWDS input based on a developed algorithm. First, the aliquot of Na$_2$CO$_3$ was carefully added and then the CO$_2$ gas was carefully injected into the water sample. The prepared bottle was shaken for 5 minutes. Then, the alkalinity and pH were measured again to compare them with the set-point alkalinity and target pH. If they did not match the procedure was repeated again.

RESULTS AND DISCUSSION

Verification of control strategy by bench-scale experiment

The variations were compared with the alkalinity and pH of sampled water before and after addition of Na$_2$CO$_3$ and CO$_2$ performing the control action in the bench-scale experiments. The alkalinities of the SWDS input were almost 40 mg L^{-1} as CaCO$_3$. For the different set points of 70, 80, 90, 100 mg L^{-1} as CaCO$_3$, the Na$_2$CO$_3$ dosage required were calculated to be 28.2, 40.3, 55.0, and 70.0 mg L^{-1} (5.63 × 10^{-4}, 8.06 × 10^{-4}, 1.1 × 10^{-3}, and 1.4 × 10^{-3} eq L^{-1}), respectively. After the Na$_2$CO$_3$ addition the alkalinities were measured to be 72.4, 81.2, 93.5, and 106.2 mg L^{-1} as CaCO$_3$. Due to the control of alkalinity the pH was increased to 9.39 ~ 9.91, which was proportional to the Na$_2$CO$_3$ dosage. The calculated CO$_2$ dosage was 17.6, 26.9, 40.1, and 60.0 mg L^{-1} (3.52 × 10^{-4}, 5.39 × 10^{-4}, 8.01 × 10^{-4}, and 1.2 × 10^{-3} eqL^{-1}), respectively, and was converted to volume unit, 0.19, 0.29, 0.43, and 0.65 ml min^{-1}, respectively. Then this CO$_2$ was added to decrease the pH. The pH was maintained between 7.93 and 8.22. One can conclude that the control algorithm was verified by the bench-scale experiment as a batch mode.

### Validation of controller at the pilot-scale experiment

For the pilot-scale experiment the water qualities of the control tank input were measured and shown in Figure 3. Calcium concentration was in the range of 40 to 90 mg L^{-1} as CaCO$_3$ which was enough for producing CaCO$_3$ by manipulating only alkalinity and pH. Therefore, the calcium was not controlled. The pH was slightly lower than 7, and it could be increased up to 8.3 due to regulation. In this condition the alkalinity should be maintained between 50 ~ 100 mg L^{-1} as CaCO$_3$, which could be estimated as satisfying the requirement of CCPP to be 0 ~ 4 mg L^{-1}. The controller was implemented and the water qualities of the control tank output were measured. Their results are shown in Figure 3. Most of the pH was maintained between 8 ~ 9 and the alkalinity was 60 ~ 80 mg L^{-1} as CaCO$_3$ except for some extreme cases. These results reasonably satisfied the expectations and were compared with the CCPP results.

Figure 4 shows that the CCPP in the control tank input, which was not controlled, was in the range of −116 ~ −4 mg L^{-1}. This was an unsaturated condition in terms of CaCO$_3$. The CCPP of its output, which was controlled, was relatively smooth as in the range of −12.2 ~ 12.8 mg L^{-1}. Many of them would have been around the 0 ~ 4 mg L^{-1} but not quite within the range. These were improved slightly after 18th September. This result might be due to some of the following reasons: The control parameter was the CCPP, but it was the secondary parameter. The calculation equation of the CCPP was somewhat non-linear as a function of the alkalinity and pH, and therefore the controller would not have been sensitive enough. Also, the time lag of the alkalinity instrument was not considered in the controller. A more precise controller for considering these effects should be developed in the near future. However, this PID controller would be useful for practical purposes.

### Effect of corrosion control based on CCPP and release of iron and zinc

In order to see the effect of corrosion control, the water quality including iron and zinc, was monitored at the tap water line of the Institute of Water Quality Research and compared with the controlled cases at the SWDS. The Institute water was supplied from another advanced water treatment plant which was similar to this advanced water treatment plant. Figure 5 shows a comparison of the CCPP variations of tap water of the institute and those at the end of the SWDS. For the uncontrolled case, the CCPP of the tap water was very low and in the range of −17.37 ~ −3.08 mg L^{-1}, with an average value of −7.77 mg L^{-1}, which had high potential
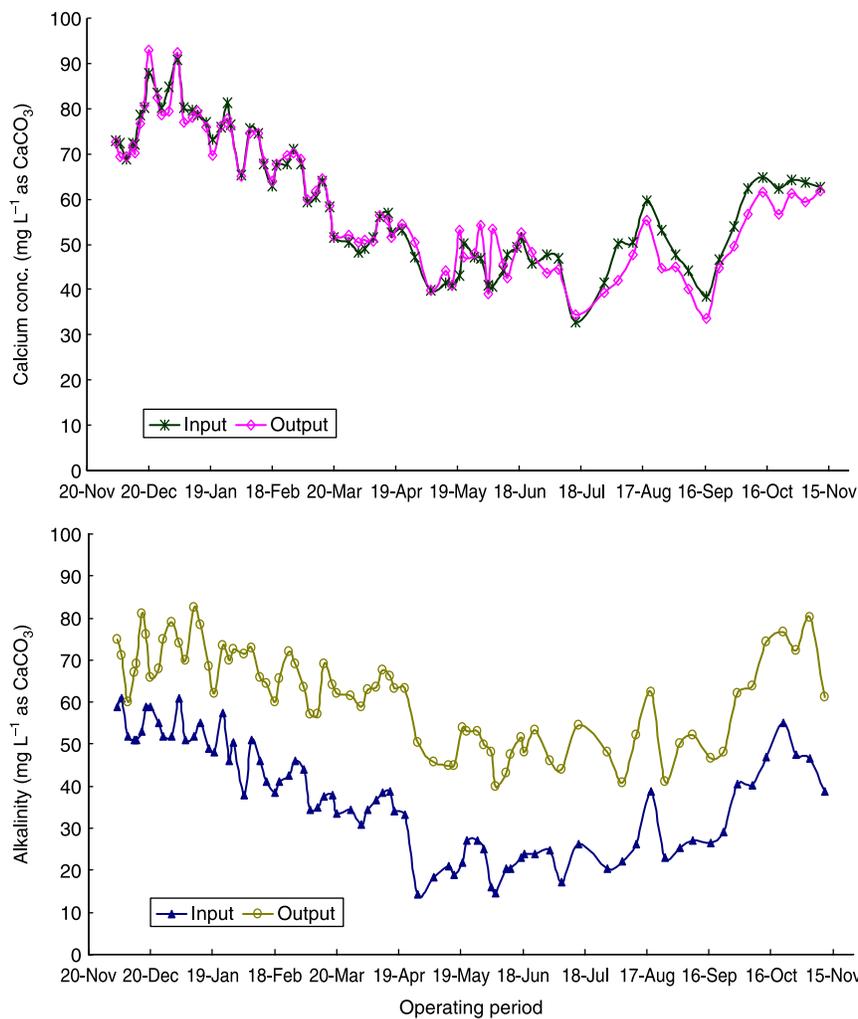
Figure 3 │ Temporal variation of alkalinity and calcium concentrations measured at the input and output of the control tank during the operating period of the pilot plant.
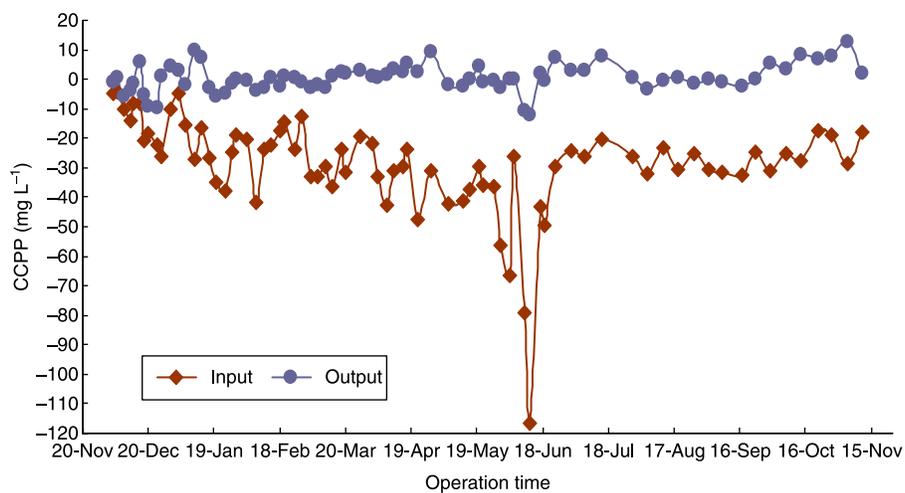
Figure 4 │ Temporal variation of CCPP measured at the input and output of the control tank during the operating period of the pilot plant.
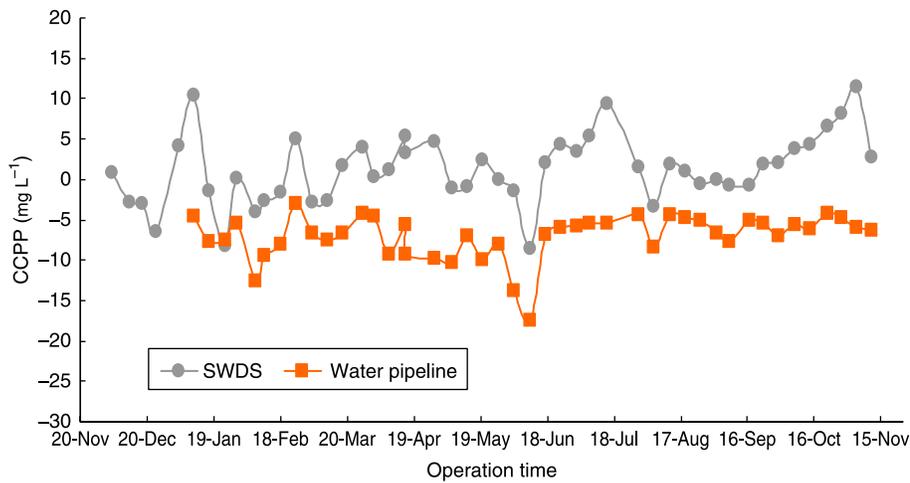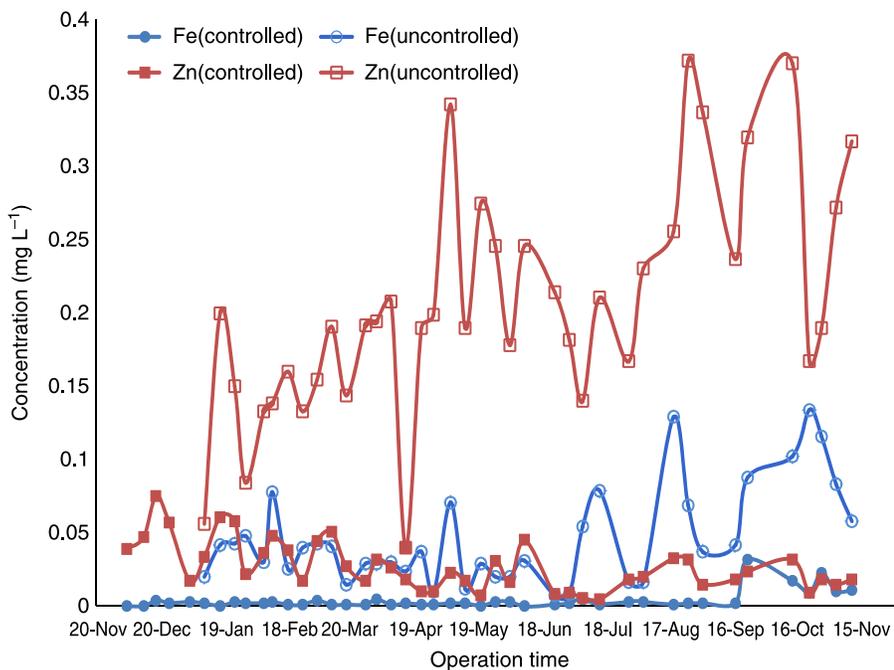
Figure 5 │ Temporal variation of CCPP measured at the end of SWDS was controlled for reducing corrosiveness of the water and at the end of water pipeline of the Institute of Water Quality Research, Busan which was not controlled.

for corrosiveness. However, for the controlled case, the CCPP of the water was $-8.64 \sim 11.52\,\mathrm{mg\,L^{-1}}$, with an average value of $0.61\,\mathrm{mg\,L^{-1}}$. The controller achieved similar results as before.

The result of that anti-corrosion effect could be evaluated by measuring the iron and zinc concentrations, because the components of the pipe material might be dissolved out according to progressive corrosion. Figure 6 shows the differences in iron and zinc concentrations of the water between the same systems described previously. In the controlled system, both heavy metal concentrations were below $0.05\,\mathrm{mg\,L^{-1}}$ except for several days out of the year. The iron and zinc concentrations in the uncontrolled cases were $0.007 \sim 0.134\,\mathrm{mg\,L^{-1}}$ and $0.04 \sim 0.372\,\mathrm{mg\,L^{-1}}$,

Figure 6 │ Temporal variation of Fe and Zn measured at the end of SWDS which was controlled for reducing corrosiveness of water and at the end of water pipeline of the Institute of Water Quality Research, Busan which was not controlled.

respectively. They were $3 \sim 7$ times higher than the controlled cases. Proper CCPP control might form a $CaCO_3$ film on the surface of the pipe and could result in a positive anti-corrosion effect.

CONCLUSIONS

It was validated that the CCPP control system of a pilot plant installed and performed according to the algorithm developed by this study could be operated to maintain a range of $0 \sim 4 \, mg \, L^{-1}$ of CCPP. The CCPP value could be controlled by manipulating the pH and alkalinity with additions of Na_2CO_3 and CO_2. The CCPP range of $0 \sim 4 \, mg \, L^{-1}$ was controlled reasonably to induce the formation of a $CaCO_3$ film on the surface of the pipeline, which provided an anti-corrosion effect. However, the on-line auto-analyzer and the PID controller's sensitivity seemed to need to be improved further. The effect of corrosion control was demonstrated by the reduced iron and zinc concentrations released from the pipe material which should indicate the presence of the $CaCO_3$ film and the efficacy of its anti-corrosion effect.

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