Korean J. Chem. Eng., **26**(1), 90-101 (2009)

Control of corrosive water in advanced water treatment plant by manipulating calcium carbonate precipitation potential

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(*Received 17 March 2008 • accepted 7 June 2008*)

Abstract−The corrosion of metal pipes in water distribution networks is a complex electrochemical and physicochemical phenomenon between a metal surface and corrosive water. The level of corrosion in water distribution systems was controlled by manipulating the calcium carbonate precipitation potential (CCPP) concentration, and the corrosive water quality was controlled in two steps within the advanced water treatment plant (AWTP) constructed at the Institute of Water Quality Research (IWQR), Busan Metropolitan City, Korea. The 1*st* control step was located before a coagulation process included on a rapid mixer, and the 2*nd* control step was located after a biological activated carbon (BAC) process. The capacity of the AWTP in IWQR was 80 m^3/day. The CCPP concentration was controlled from the calcium hardness, alkalinity, and pH by adding calcium hydroxide ($Ca(OH)_2$), sodium carbonate (Na_2CO_3), and carbon dioxide (CO_2) in the above two steps. A CCPP control system was installed and operated according to the developed algorithm to maintain a CCPP range of 0-4 mg/L. The CCPP range was reasonably controlled to induce the formation of a $CaCO_3$ film on the surface of the simulated water distribution system (SWDS). From the result of the corrosive water control, the CCPP formed greater than 0.0 mg/L. The crystalloid structure of the scale produced by CCPP control in the inner surface of pipe was zinc carbonate hydroxide hydrate ($Zn_4CO_3(OH)_6 \cdot H_2O$).

Key words: Corrosive Water, Corrosion Control, CCPP, BAC, Water Pipe

INTRODUCTION

The corrosion of metal pipes in water distribution networks is a complex electrochemical and physicochemical phenomenon between a metal surface and corrosive water, which cannot always be eliminated but can usually be controlled in a cost-effective manner [1,2]. The corrosiveness of the tap water depends on chemical factors, such as pH, alkalinity, buffer intensity, dissolved oxygen and total dissolved solids (TDS), and physical properties, such as temperature, flow and velocity, as well as the nature of the pipe material [3-5]. In the water treatment process, pH, alkalinity and calcium hardness can be manipulated for the removal of color and corrosion control to prevent internal corrosion of a water distribution system [6,7].

There are several kinds of corrosion control methods, including corrosion indexes (e.g., Langelier Saturation Index (LSI), the Larson Index (LI), the Ryznar Index (RI), Aggressive Index (AI), Driving Force Index (DFI), Momentary Excess (ME) and Calcium Carbonate Precipitation Potential (CCPP)), corrosion control inhibitors (e.g., orthophosphates, molecularly dehydrated polyphosphates, and bimetallic (zinc-containing) phosphates) and water quality controls [1-4,8].

In general, treated tap water is transported from waterworks to indoor taps, where the water is supplied via water distribution pipelines. Water distribution systems in Korea are organized into metal pipes, such as steel pipes (SP), cement mortar lining ductile cast iron pipes (CML-DCIP), galvanized steel pipes (GSP), stainless steel pipes (STS), and copper pipes (CP) [9]. In potable water pipes made from metal, materials compounded with several heavy metals such as iron, zinc, copper and lead, are released from the inner surface of metal pipes [10], with the induction of toxins and red colored water because oxygen and hydrogen ions (H^+) in the water corrode the inner surface of metal pipes [11]. Therefore, corrosive water from water treatment plants can cause problems, such as health hazards, taste, color and higher utility pumping costs, due to the obstruction of water flow by the corrosion products deposited on the pipe surface in water pipelines and plumbing systems [2,12,13]. The most common symptom of corrosion problems within a water system is customer complaints with regard to “red water” and “discolored water” [3,14,15].

One corrosion control method occurs when the CCPP concentration of corrosive water is controlled by water quality parameters, such as pH, alkalinity and calcium hardness, which can induce the formation of calcium carbonate compounds in the internal wall of water pipes. The CCPP is defined as the quantity of calcium carbonate ($CaCO_3$) that can be theoretically precipitated from oversaturated waters or dissolved by undersaturated waters during equilibration. The CCPP is negative for undersaturated waters, zero for saturated waters and positive for oversaturated waters [5,16-19], and is a parameter that quantifies the mass of $CaCO_3$ and the index best suited to describe $CaCO_3$ precipitation and dissolution [5,20]. The CCPP can be calculated from the pH, alkalinity, calcium hardness, TDS

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and temperature, or determined by using the Rothberg, Tamburini, and Winser (RTW) model [21].

The AWTP by a BAC filtration process can reduce the concentration of dissolved organic carbon (DOC) in raw water more than a general water treatment process without the BAC procedure [22-24]. The film formed on the inner surface of water pipes by natural organic matter (NOM) included in the DOC components plays some role in corrosion prevention [25]. The NOM in the water can also be reduced by DOC reduction through the BAC process. Therefore, the aim of this study was to develop a control technology and confirm the control possibility for corrosion prevention in a water distribution system by the CCPP concentration after DOC reduction through the BAC process. The AWTP included pre-chlorination, pre-ozonation, coagulation, flocculation, sedimentation, sand filtration, post-ozonation, BAC, post-chlorination, and reservoir processes.

The CCPP concentration was manipulated before reaching the water distribution system by controlling the water quality using the following two processes. The 1st control step involved manipulating the calcium hardness and pH by adding a quantity of $Ca(OH)_2$ and CO_2 before the coagulation process. The 2nd control step involved controlling the required CCPP concentration by adding a quantity of Na_2CO_3 and CO_2.

In each water treatment process unit, the water quality is monitored and controlled by on-line automatic measuring instruments and the developed corrosion control system. The simulated water distribution system (SWDS) was connected to the above AWTP. An examination of the inner surface and analyses of the components of the SWDS for corrosion control were conducted.

MATERIALS AND METHODS

1. The Advanced Water Treatment Process for Corrosive Water Quality Control System

Fig. 1 shows the composition of the advanced water treatment pilot plant (AWTPP) and corrosive water quality control system. The AWTPP, which was located at the IWQR, Busan Metropolitan City, Korea, consisted of various treatment stages, including pre-ozonation, coagulation, sedimentation, sand filtration, post-ozonation and BAC, with a capacity of 80 m^3/day. The system for the control of the corrosiveness of water was installed into the AWTPP by using a proportional integral derivative (PID) controller.

An automatic control system for the control of corrosive water quality quantitatively governs the water quality by the injection of chemicals according to variations in the raw water quality during the water treatment process. The control algorithms were developed from the chemical dosage founded on theoretical calculations. This control system, based on a personal computer (PC), was designed to organize the process control logics. The control system was divided into two stages for the advanced water treatment process. The first control strategy was carried out between the pre-ozone and post-ozone processes, and the second was placed between the BAC process and final treated water reservoir.

The main computer system for the control of the corrosive water quality consisted of a control program and man-machine interface (MMI), which is able to monitor in real time and send the data signals to a programmable logic controller (PLC). The data from on-line measuring instruments, such as pH, calcium hardness, alkalinity, temperature and TDS, were analyzed to the PLC, with calculations performed on a computer using the corrosion control algorithms.

Specific symbols were marked according to the monitoring points and measuring or detecting instruments for the AWTPP and corrosion control system. The list of symbols and contents is shown in Table 1.

2. Control Algorithm and Computing Chemical Dosage

In the 1st control stage, the control strategy established pH and calcium hardness as the target water parameters. The 2nd control strategy for the CCPP concentration control targeted pH and alkalinity as the parameters of the BAC effluent. The control algorithms

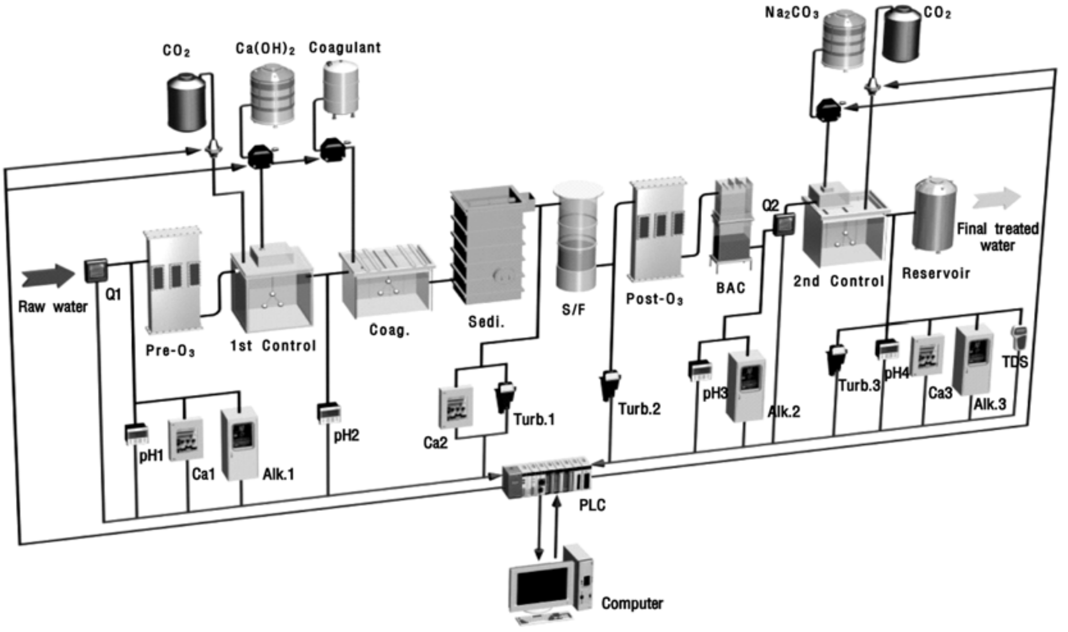

Fig. 1. A schematic diagram of the corrosive water quality control system in an advanced water treatment pilot plant (AWTPP).

Table 1. List of the monitoring instruments for the advanced water treatment process

Symbols	Details	Unit	Monitoring points
Q1	Water flow rate	m^3/day	Raw water; before pre-ozonation process
Q2			BAC effluent; before 2nd control tank
pH1	Potential of hydrogen	-	Raw water; before pre-ozonation process
pH2			Controlled water; after 1st control tank
pH3			BAC effluent; before 2nd control tank
pH4			Controlled water; after 2nd control tank
Ca1	Calcium hardness	mg/L as $CaCO_3$	Raw water; before pre-ozonation process
Ca2			Settling tank effluent; before sand-filtration process
Ca3			Controlled water; after 2nd control tank
Alk.1	Alkalinity	mg/L as $CaCO_3$	Raw water; before pre-ozonation process
Alk.2			BAC effluent; before 2nd control tank
Alk.3			Controlled water; after 2nd control tank
Turb.1	Turbidity	NTU	Settling tank effluent; before sand-filtration process
Turb.2			Sand filter effluent; before post-ozonation process
Turb.3			Controlled water; after 2nd control tank
TDS	Total dissolved solid	mg/L	Controlled water; after 2nd control tank

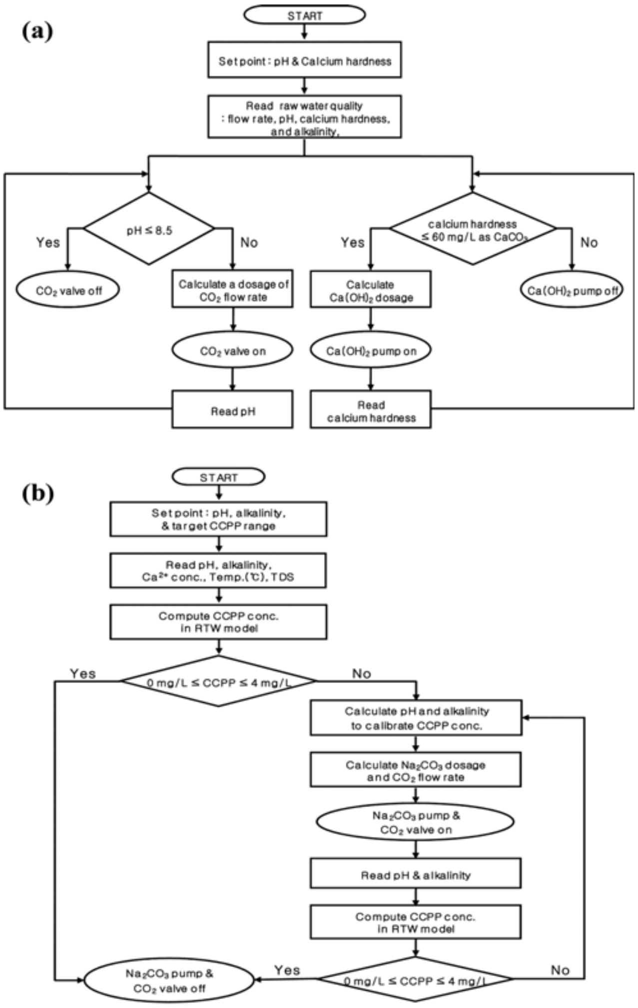

Fig. 2. The control algorithms for the corrosion control system: (a) 1st control stage for the control of the pH and calcium hardness, and (b) 2nd control stage for the control of the pH, alkalinity and CCPP concentration.

for each control steps are shown in Fig. 2. To increase the calcium hardness when that of the raw water was lower than a set point, as well as to adjust the pH to the target value, $Ca(OH)_2$ and CO_2 were added into the tank of the 1st control stage. Na_2CO_3 and CO_2 were injected into the tank at the 2nd control stage to increase the alkalinity and to control the pH at the given target values. Therefore, the control objective was to prevent corrosion of the pipelines in a water distribution system by maintaining the CCPP within the range of 0.0-4.0 mg/L at the input to the SWDS. The temperature and TDS, as water factors, were difficult to manipulate.

The reactive components were assumed to be water (H_2O), hydrogen ions (H^+), hydroxyl ions (OH^-), carbon dioxide (CO_2), carbonic acid (H_2CO_3), bicarbonate ions (HCO_3^-), carbonate ions (CO_3^{2-}), and calcium ions (Ca^{2+}) [5,17].

The required amount of $Ca(OH)_2$ and Na_2CO_3 was calculated using Eq. (1) to Eq. (3), as follows:

$$Ca(OH)_2\ \text{required [mole/L]}=[\text{Alk.}]_{desired}-[\text{Alk.}]_{initial}=\Delta[\text{Alk.}] \tag{1}$$

$$[\text{Alk.}]_{desired}=[\text{Alk.}]_{initial}-[Ca^{2+}]_{initial}+[Ca^{2+}]_{desired} \tag{2}$$

where, $[\text{Alk.}]_{initial}$=alkalinity of raw water
$[Ca^{2+}]_{initial}$=calcium hardness of raw water
$[Ca^{2+}]_{desired}$=target concentration of calcium hardness

If the $[Ca^{2+}]_{initial}$ was more than the $[Ca^{2+}]_{desired}$ in the influent water than those of raw water, the $[Ca^{2+}]_{desired}$ and $[Ca^{2+}]_{initial}$ were computed as being equal. The $Ca(OH)_2$ would then not be required to control the calcium hardness.

The alkalinity was calculated according to the previously published procedures [26].

$$Na_2CO_3\ \text{required [mole/L]}=[\text{Alk.}]_{desired}-[\text{Alk.}]_{initial}=\Delta[\text{Alk.}] \tag{3}$$

where, $[\text{Alk.}]_{desired}$=target concentration of alkalinity
$[\text{Alk.}]_{initial}$=alkalinity of BAC effluent
$\Delta[\text{Alk.}]$=variation of alkalinity concentration

The pH was increased by the addition of $Ca(OH)_2$ and Na_2CO_3.

Table 2. The input contents target values in each control stage

Division	Symbols	Unit	Set point	Contents
1st control stage	DECa1	mg/L as $CaCO_3$	60	Target calcium hardness
	DEpH1	-	8.5	Target pH
	Lime	%	3.0	$Ca(OH)_2$ concentration
	Coagulant	mg/L	40	Coagulant concentration
2nd control stage	DEAlk.2	mg/L as $CaCO_3$	66, 68	Target alkalinity
	DEpH2	-	8.2	Target pH
	Soda ash	%	7.0	Na_2CO_3 concentration
	CCPP	mg/L	0.0-4.0	CCPP concentration

To decrease the pH when near to the target value, CO_2 was required for pH control. The required amount of CO_2 gas was calculated from the following equation:

$$CO_2 \text{ gas required [mole/L]} = [C_T]_{desired} - [C_T]_{initial} = \Delta[C_T] \qquad (4)$$

where, $[C_T]_{desired}$=target concentration of C_T after CO_2 added to water
$[C_T]_{initial}$=C_T concentration after $Ca(OH)_2$ or Na_2CO_3 added to water
$\Delta[C_T]$=variation of concentration according to C_T by CO_2

Since only a small fraction of the total CO_2 dissolved in water is hydrated to H_2CO_3, it is convenient to sum the concentrations of dissolved CO_2 and H_2CO_3 to define a new concentration term, $H_2CO_3^*$. The total carbonic species concentration in solution is usually represented by C_T and defined in terms of a mass balance expression:

$$C_T \text{ (total carbonate carbon)} = [H_2CO_3^*] + [HCO_3^-] + [CO_3^{2-}] \qquad (5)$$

$$[C_T] = \frac{1}{\alpha_0}\left(\frac{2[\text{Alk.}] - \frac{K'_W}{[H^+]} + [H^+]}{\frac{2K'_1K'_2}{[H^+]^2} + \frac{K'_1}{[H^+]}}\right) \qquad (6)$$

$$\alpha_0 = \frac{1}{1 + \frac{K'_1}{[H^+]} + \frac{K'_1K'_2}{[H^+]^2}} \qquad (7)$$

$$K'_1 = \frac{K_1}{(\gamma_m)^2} = \frac{[H^+][HCO_3^-]}{[H_2CO_3^*]} \qquad (8)$$

$$K'_2 = \frac{K_2}{\gamma_D} = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} \qquad (9)$$

$$K'_W = \frac{K_W}{(\gamma_m)^2} = [H^+][OH^-] \qquad (10)$$

where, γ=activity coefficient, with the subscripts m and D representing the absolute value of the oxidation number of the chemical species (e.g., γ_m represents the activity coefficent for monovalent ions, γ_D represents the activity coefficient for divalent ions)

The equilibrium constants K_1, K_2, and K_W may be adjusted for temperature by applying the following relationships [27]:

$$pK_1 = \frac{17{,}052}{T} + 215.21(\log T) - 0.12675(T) - 545.56 \qquad (11)$$

$$pK_2 = \frac{2902.39}{T} + 0.02379(T) - 6.498 \qquad (12)$$

$$pK_W = \frac{4787.3}{T} + 7.1321(\log T) + 0.010365(T) - 22.801 \qquad (13)$$

where, T=the solution temperature is in degrees Kelvin

3. The Operating Method of Pilot Plant and Control System

The raw water used in this study was obtained from the Nakdong River, Korea. The control strategies for corrosive water in the AWTPP and the target values are shown in Table 2. The treated water quality as reported in Table 2 was considered to satisfy the standard for drinking water in Korea. The CCPP concentration was automatically calculated by the RTW model ver. 3.0 [21] from automatically analyzed data, such as calcium hardness, alkalinity, pH, TDS and temperature. The RTW model was linked to the developed corrosion control program.

4. The Instruments and Equipment in Advanced Water Treatment Process

4-1. The 1st Control Tank

When approximately 3% $Ca(OH)_2$ was added to the 1st control tank before the coagulation process for calcium hardness control, the water became turbid as a result of the low solubility of $Ca(OH)_2$ and the pH increased. This higher pH needed to be reduced for the coagulation process to proceed. Acidic CO_2 gas from a cylinder was added to decrease the pH, which resulted in a slight decrease in turbidity. However, fine particles were still suspended in the water due to the low solubility of $Ca(OH)_2$. These fine particles were removed completely through the sedimentation and sand filtration process.

The clean water treated by transit through the above processes was flowed to the BAC process. For the above reason, the calcium hardness could not be controlled at the BAC unit process.

4-2. The Constitution of Equipment for Carbon Dioxide Control

The constitution for the control of carbon dioxide included a gas cylinder, manometer, regulator of pressure, indicator and mass flow controller (MFC). The amount of CO_2 in the cylinder was confirmed by using the manometer, with the pressure preserved by the regulator. The MFC transmitted the signal from the PLC, which controlled the proper injection of CO_2. The CO_2 was injected via diffuser set up in the first and second control tanks.

4-3. The Facilities to Add the Calcium Hydroxide ($Ca(OH)_2$)

To control the calcium hardness of corrosive water, the system for the addition of $Ca(OH)_2$ was composed of tanks and pumps for the solution and circulation, respectively. A tank installed with mixer was used to dilute the $Ca(OH)_2$ solution by about 3% (±2%). If the distance between the solution tank and chemicals injection point was long, the $Ca(OH)_2$ would form sediment due to its low solubility. Therefore, a circulation tank and pump were required to save the quantity of the injected chemicals.

4-4. The 2^{nd} Control Tank

If the alkalinity of the BAC effluent was lower than the target alkalinity range, a Na_2CO_3 solution was added to the 2^{nd} control tank to increase the alkalinity to the target range. Because the pH is increased by adding Na_2CO_3, the pH in the 2^{nd} control tank is higher than the target pH range. Therefore, the pH was controlled by adding acidic CO_2 gas. When the alkalinity of the BAC effluent was higher than the target alkalinity range, the alkalinity and pH of BAC effluent was controlled by adding acidic CO_2 gas until the required CCPP concentration range was reached.

4-5. The Additional Equipment for Sodium Carbonate (Na_2CO_3)

To control the alkalinity of the BAC effluent, the equipment for the injection of Na_2CO_3 was installed with an automatic melter, a circular pump, recycling tank and a quantitative dosage pump. An automatic Na_2CO_3 powder melter to prepare the 7% Na_2CO_3 solution has a storage tank equipped with stirrer. The dosage was determined from the control signals calculated from the PID controller and main control computer.

4-6. Automatic Control System and Measuring Instrument

Several sets of data were obtained from automatic analysis of the pH/temperature (alpha-pH1000, EUTECH Instruments), total dissolved solids (CyberScan 200, USA) and turbidity (1720E Turbidimeter, HACH) using on-line sensors, which were able to collect the monitoring data in real time. The water qualities obtained from the measuring instruments, such as calcium hardness and alkalinity, were used to automatically analyze the data transferred online. The process for measuring the water quality was based on the standard methods to analyze the quality of potable water. The control system for corrosive water was composed of the MMI software, which can be used to control and monitor advanced water treatment plants containing ozone and BAC processes. The state of the water quality in each unit process was monitored by on-line systems in real time.

5. The Simulated Water Distribution System (SWDS)

The simulated water distribution system (SWDS) was composed of a water main pipe, a distributing pipe, a service pipe and an indoor pipe, and connected to the AWTPP, as shown in Fig. 3. The SWDS selected the materials from the water distribution systems used in Busan City. The materials of a main water pipe, a distributing pipe, a service pipe and an indoor pipe were constructed of steel, ductile cast iron pipe (DCIP), stainless steel (STS304), copper and galvanized steel, respectively. The flow velocity of controlled water in the SWDS was maintained continuously with a spontaneous flow. The specifications of the SWDS are shown in Table 3. The length of the SWDS was about 150 m, with those of each pipe designed so as to organize the ratio of material could be considered when the water distribution pipeline was filed. Because the water stored in the reservoir flowed into the SWDS under gravity, the flow velocities of the treated water in the SWDS were controlled according to the diameter and length of each kind of pipe.

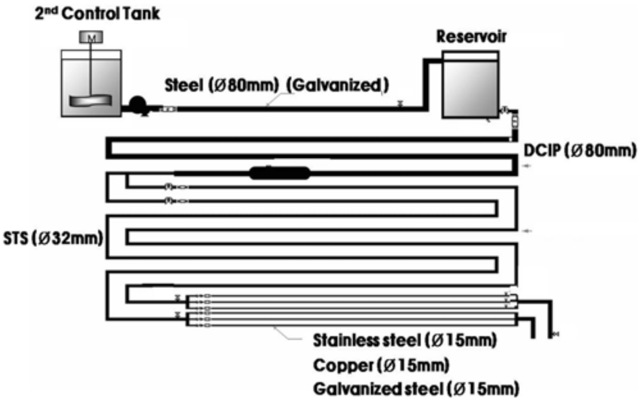

Fig. 3. A schematic diagram of the simulated water distribution system (SWDS).

6. The Analysis of Inner Surface about SWDS

Visual observations and scanning electron microscopy (SEM) were used to observe the structure of the inner surface of a pipe due to scale formed by corrosion products in the controlled corrosive water. Energy dispersive X-ray spectroscopy (EDX) was used for an elemental analysis or chemical characterization of the scale on the inner surface of the pipe. X-ray diffraction (XRD) was then used to reveal the crystallographic structure, chemical composition and physical properties of the materials and thin calcium carbonate films. The SWDS sample, where water had been passing for approximately 36 months, was used for the analysis.

RESULTS AND DISCUSSION

1. The Characteristics of Raw Water and BAC Effluent

During the period of the pilot plant scale experiments, the characteristics of the raw water and BAC effluent were measured more than 31 times. Table 4 shows the water quality factors for the raw

Table 3. The composition of the simulated water distribution system (SWDS)

Classification	The kind of pipe	The diameter/ length of pipe	The flow velocity	The retention time	Type
The water main pipe	Steel pipe	80 mm/23.4 m	2.5-2.6 m/s	3 min. 15 sec	Continued flow
The distributing pipe	Ductile cast iron pipe (DCIP)	80 mm/46.5 m	0.15-0.2 m/s	6 min. 29 sec	
The service pipe	Stainless steel pipe (STS304)	32 mm/71.8 m	0.35-0.45 m/s	30.5 sec	
The indoor pipe	Copper pipe Stainless steel pipe (STS304) Galvanized steel pipe	15 mm/9.0 m	0.5-0.8 m/s	2.7 sec	

Table 4. Water quality characteristics of the raw and BAC effluent

Contents	Raw water (1st control)			BAC effluent (2nd control)		
	Min.	Max.	Mean	Min.	Max.	Mean
pH	7.62	9.81	8.78	7.00	7.54	7.24
Temp. (°C)	1.8	15.7	8.5	3.5	16.4	9.1
Ca^{2+} hardness (mg/L as $CaCO_3$)	62.3	80.4	72.5	64.3	82.1	75.2
Alkalinity (mg/L as $CaCO_3$)	66.3	78.4	70.6	51.4	66.0	57.1
Turbidity (NTU)	1.1	111.0	15.5	0.07	0.20	0.12
SS (mg/L)	1.6	142.8	16.4	0.0	2.0	0.37
TDS (mg/L)	232	389	313	226	405	303
Total hardness (mg/L as $CaCO_3$)	72.0	160	109	-	-	-
Residual chlorine (mg/L)	0.0	0.8	0.1	-	-	-
UV254 (/cm)	0.03	0.07	0.05	0.01	0.04	0.02
THMs (mg/L)	N/D	N/D	N/D	N/D	N/D	N/D
TTHMFP (mg/L)	0.09	0.25	0.16	0.04	0.08	0.06
TOC (mg/L)	1.13	4.50	3.01	0.84	2.08	1.28
DOC (mg/L)	0.94	4.40	2.88	0.67	2.04	1.19
Ca^{2+} ion (mg/L)	22.4	33.5	27.6	21.4	33.5	28.2
SO_4^{2-} ion (mg/L)	37.0	93.0	70.0	-	-	-
Cl^- ion (mg/L)	30.0	64.0	45.0	-	-	-
Na (mg/L)	30.0	52.0	43.0	-	-	-
Zn (mg/L)	0.004	0.078	0.022	-	-	-
Fe (mg/L)	0.00	5.11	0.49	-	-	-
Mn (mg/L)	0.01	0.92	0.09	-	-	-
Al (mg/L)	0.09	4.44	0.44	-	-	-
CCPP (mg/L)	−6.37	24.47	6.21	−24.65	−9.13	−16.90
LSI	−0.63	1.53	0.50	−1.37	−0.83	−1.14

water and BAC effluent. The ranges of the water quality factors for raw water were pH 7.62-9.81 (mean 8.78), temperature 1.8-15.7 °C (mean 8.5 °C), calcium hardness 62.3-80.4 mg/L as $CaCO_3$ (mean 72.5 mg/L as $CaCO_3$), alkalinity 66.3-78.4 mg/L as $CaCO_3$ (mean 70.6 mg/L as $CaCO_3$), TDS 232-389 mg/L (mean 313 mg/L) and turbidity 1.1-111 NTU (mean 15.5 NTU). The ranges of the CCPP concentration and LSI were −6.37-24.47 mg/L (mean 6.21 mg/L) and −0.63-1.53 (mean 0.5), respectively. The values of the water quality factors for raw water, from minimum to maximum, can have wide fluctuation. The raw water used in this study was obtained from the Nakdong River, Korea. Due to the considerable changes in the water characteristics, control of the corrosive water by an automatic monitoring and controlling system is required.

The ranges of the water quality factors for the BAC effluent were pH 7.00-7.54 (mean 7.24), temperature 3.5-16.4 °C (mean 9.1 °C), calcium hardness 64.3-82.1 mg/L as $CaCO_3$ (mean 75.2 mg/L as $CaCO_3$), alkalinity 51.4-66.0 mg/L as $CaCO_3$ (mean 57.1 mg/L as $CaCO_3$), TDS 226-405 mg/L (mean 303 mg/L) and turbidity 0.07-0.20 NTU (mean 0.12 NTU). The ranges of the CCPP concentration and LSI were −24.65∼−9.13 mg/L (mean −16.90 mg/L) and −1.37∼−0.83 (mean −1.14), respectively. The differences in the water quality values for the BAC effluent did not change much compared to those for raw water, but the water quality factors, such as pH, alkalinity, CCPP concentration and LSI, were all low. The BAC effluent for advanced water treatment takes strong corrosive water at the above CCPP concentration and LSI values, and the corrosive water was flowed into the water distribution pipeline; therefore, the water quality has to be manipulated to prevent corrosion of metal pipes.

2. Monitoring the Water Quality in Each Unit Process

On inspecting the variety of water quality factors according to the chemical dosage, the pH of the raw water was 7.87, but a range of 7.24-7.54 was regularly maintained after coagulation to the BAC filtration process. The pH of the final controlled water was increased to 8.43. The trend with the alkalinity was similar to the pH, with that of raw water being 65.0 mg/L as $CaCO_3$. The range of alkalinities after coagulation to the BAC filtration process was regularly maintained at 50.2-54.3 mg/L as $CaCO_3$. The alkalinity of the final treated water in the 2nd control stage was increased to 64.1 mg/L as $CaCO_3$ by the addition Na_2CO_3. The calcium hardness in each unit process varied very little, with the range maintained at 69.0-70.9 mg/L as $CaCO_3$. Because the calcium hardness in the coagulation process was over the target concentration (60 mg/L as $CaCO_3$) for the examination of corrosion control in AWTPP, no $Ca(OH)_2$ was added. The turbidity and SS were almost removed after the sand filtration process. In the 2nd control stage, the turbidity did not increase after the injection of Na_2CO_3; therefore, Na_2CO_3 is good for controlling the pH and alkalinity in the control of corrosive water. All other items within the water quality analysis are shown in Table 5.

Fig. 4(a) shows the movement in the water factors, such as pH, temperature, alkalinity and calcium hardness, for each unit in the water treatment process. After the BAC unit process, the pH and

Table 5. The water quality obtained with the unit water treatment process

Analysis items	Raw water			Coagulation			Sedimentation			Sand-filtration		
	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean
pH	7.62	9.81	8.78	7.08	7.57	7.29	7.07	7.57	7.28	7.12	7.55	7.33
Temp. (°C)	1.8	15.7	8.5	2.0	15.7	8.5	2.0	15.6	8.5	2.4	15.6	8.5
Ca^{2+} hardness (mg/L as $CaCO_3$)	56.0	83.7	68.9	53.8	80.0	69.2	55.9	80.1	70.2	54.8	82.5	70.9
Alkalinity (mg/L as $CaCO_3$)	56.0	74.0	65.0	46.0	65.0	54.3	45.0	65.0	53.5	46.0	64.0	53.2
Turbidity (NTU)	1.1	111.0	15.5	5.64	25.2	11.7	0.20	1.86	0.84	0.08	0.36	0.15
TTHM (mg/L)	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D
TTHMFP (mg/L)	0.09	0.25	0.16	0.08	0.16	0.12	0.08	0.13	0.11	0.03	0.11	0.08
TOC (mg/L)	1.1	4.5	3.0	1.5	3.8	2.4	1.5	3.7	2.2	1.4	3.6	2.1
DOC (mg/L)	0.9	4.4	2.9	1.5	3.4	2.3	1.5	3.2	2.1	1.3	3.2	2.0
UV254 (/cm)	0.03	0.07	0.05	0.03	0.07	0.04	0.03	0.06	0.03	0.01	0.05	0.03
TDS (mg/L)	232	389	313	242	412	324	224	397	309	217	395	307
SS (mg/L)	1.6	142.8	16.4	12.4	29.6	21.1	0.4	16.0	3.9	0.0	2.0	0.5

Analysis items	Post-ozonation			BAC-filtration			Final treated water (2^{nd} control stage)		
	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean
pH	7.23	7.88	7.54	7.00	7.54	7.24	7.96	8.74	8.43
Temp. (°C)	3.2	16.1	8.9	3.5	16.4	9.1	3.6	16.3	9.3
Ca^{2+} hardness (mg/L as $CaCO_3$)	54.4	81.8	70.7	53.6	83.8	70.4	54.3	82.7	69.0
Alkalinity (mg/L as $CaCO_3$)	44.0	55.0	51.0	44.0	58.0	50.2	55.0	77.0	64.1
Turbidity (NTU)	0.08	0.28	0.13	0.07	0.20	0.12	0.07	0.18	0.10
TTHM (mg/L)	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D
TTHMFP (mg/L)	0.04	0.12	0.07	0.04	0.08	0.06	0.04	0.11	0.06
TOC (mg/L)	1.4	3.4	2.0	0.8	2.1	1.3	0.8	2.4	1.3
DOC (mg/L)	1.1	3.2	1.9	0.7	2.0	1.2	0.7	2.1	1.2
UV254 (/cm)	0.01	0.05	0.03	0.01	0.04	0.02	0.01	0.03	0.01
TDS (mg/L)	218	382	306	226	405	303	245	442	326
SS (mg/L)	0.0	2.0	0.4	0.0	2.0	0.4	0.0	0.4	0.1

alkalinity were most significantly increased, since these factors were importantly correlated with the CCPP concentration. The increases in the turbidity and accumulation of sludge in the coagulation and sedimentation process were induced by the injection of $Ca(OH)_2$ and CO_2 in 1^{st} control stage. The pH and alkalinity of final treated water in the 2^{nd} control stage were 8.4 and 69.9 mg/L as $CaCO_3$ respectively, according to the injected amounts of Na_2CO_3 and CO_2.

Fig. 4(b) shows the variations in the CCPP concentration and LSI in each unit water treatment process. The CCPP of the influent raw water ranged from –6.64 to 23.98 mg/L and the mean was 3.66 mg/L; however, the results revealed that the treated water had strong corrosiveness when passed through the water treatment process from coagulation to the BAC filtration process, since the mean of CCPP concentration was −13.2 mg/L. However, the CCPP concentration of the final treated water was reliably controlled to a mean of 0.84 mg/L via the 2^{nd} control stage. In the general case of tap water, the range of the CCPP concentration of the BAC effluent was −23.8~ −7.8 mg/L (mean −15.7 mg/L). Therefore, the water factors, such as pH, alkalinity and CCPP, were decreased during the water treatment process, but it was possible that those could be controlled to levels within non-corrosive water by using the developed corrosion control system.

3. The Result of pH and Calcium Hardness Control in 1^{st} Control Stage

To control the pH and calcium hardness in the 1^{st} control stage, chemicals, such as $Ca(OH)_2$ and CO_2, were injected before the coagulation process. The amount of CO_2 injected ranged from about 0.0 L/day to 201.6 L/day (mean 64.1 L/day). Because the calcium hardness of the influent water was higher than the target concentration, no $Ca(OH)_2$ was injected during the test. The amount of coagulant added ranged from 1.26 L/day to 3.16 L/day (mean 2.15 L/day).

Fig. 5(a) shows the variation in the pH according to the control strategy in the 1^{st} control stage. The pH value of the raw water pH (pH1) was confirmed by the controlled water pH (pH2) after the 1^{st} control tank, which was detected by an automatic measuring instrument. The pH1 range was about 7.60-9.67 (mean 8.82) and that of pH2 was about 7.74-9.01 (mean 8.41), as a result of the control of the target pH (demanded pH, DEpH1). An error range for DEpH1 8.5 was 0.002-0.108 (mean 0.045) which was only computed about CO_2. It could be verified that CO_2 was controlled when pH1 was more over than DEpH1 8.5 into the 1^{st} control tank (Fig. 5(a)).

Fig. 5(b) shows the variation in the calcium hardness according to control condition in the 1^{st} control stage. The result of the con-

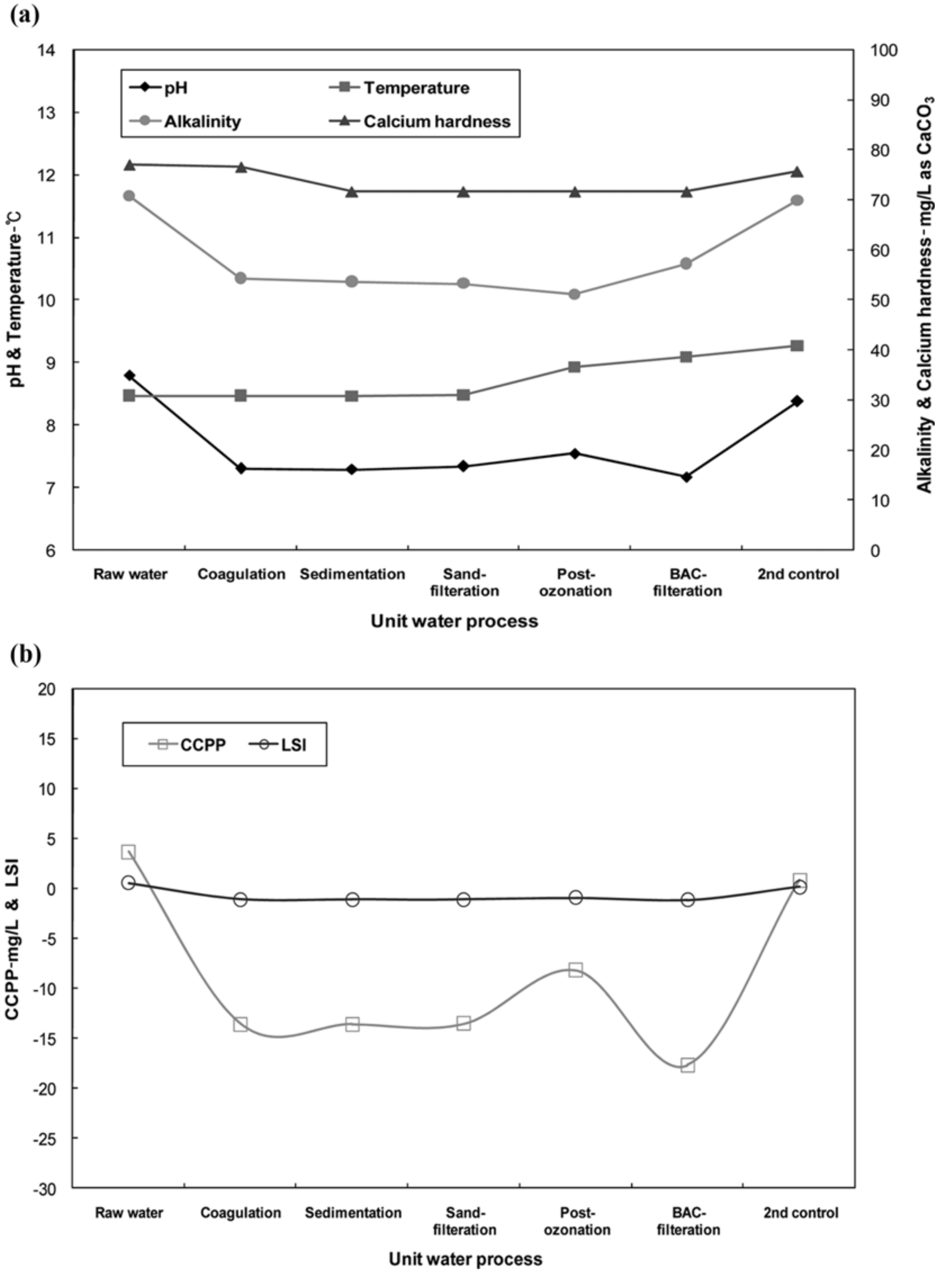

Fig. 4. The variation in each unit process: (a) the water quality factors, such as pH, alkalinity, calcium hardness and temperature, and (b) the CCPP concentration and LSI.

trolled calcium hardness for raw water (Ca1) was confirmed from the controlled water calcium hardness (Ca2) of the settling tank effluent prior to the sand filtration process. The concentration range of Ca1 was about 62.32-80.37 mg/L as $CaCO_3$ (mean 72.49 mg/L as $CaCO_3$) and that of Ca2 after the 1st control stage was 62.54-81.0 mg/L as $CaCO_3$ (mean 71.65 mg/L as $CaCO_3$); therefore, there was no change between Ca1 and Ca2. The trend of the variation in Ca2 was similar to that for Ca1. Since the calcium hardness of Ca1 was more than the target calcium hardness (demanded calcium hardness, DECa1); 60 mg/L as $CaCO_3$, no $Ca(OH)_2$ was injected by the corrosion control system.

4. The Variation of Controlled pH and Alkalinity in 2nd Control Stage

For the control of corrosive water, water quality factors, such as

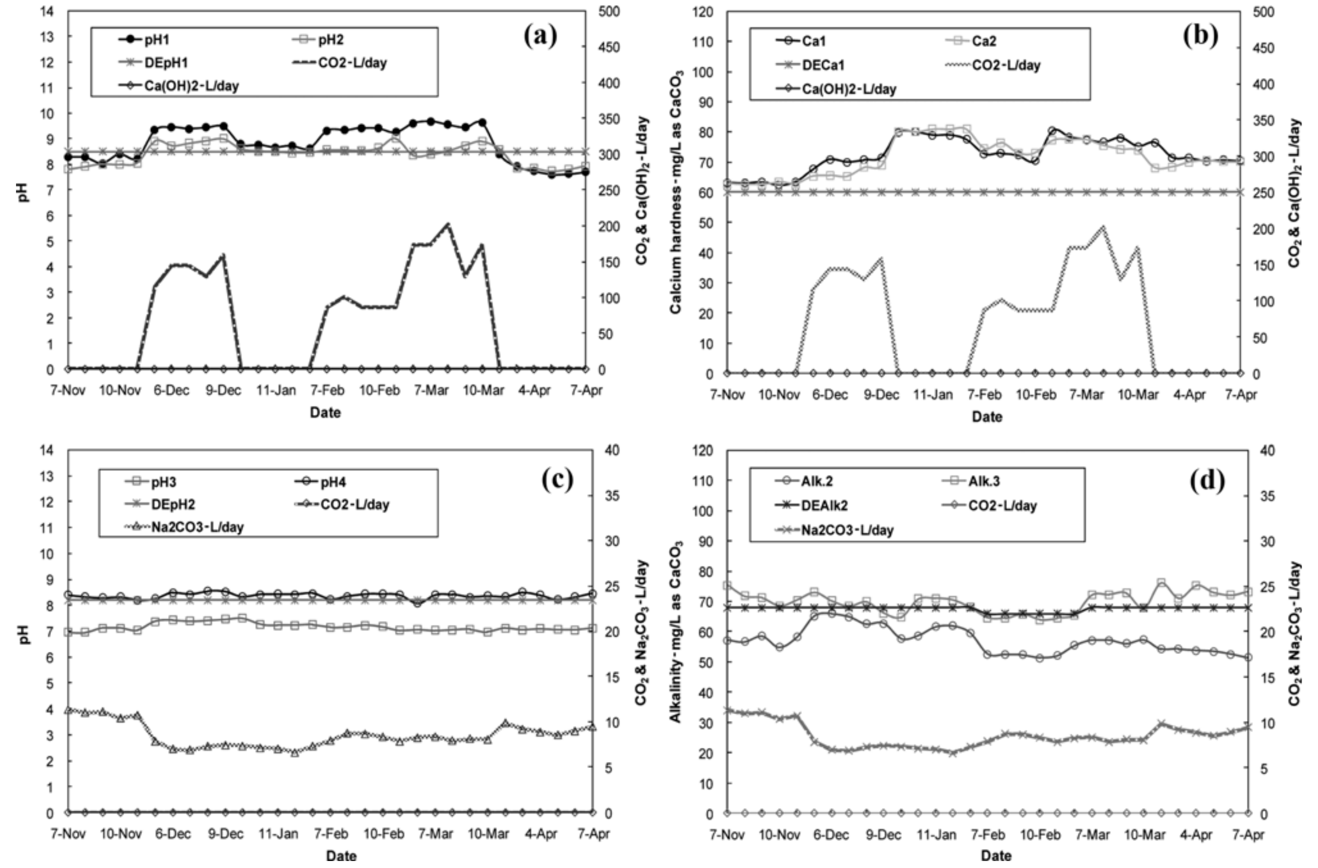

Fig. 5. The results of water quality control: (a) pH and (b) calcium hardness control in the 1st control stage and (c) pH and (d) alkalinity control in the 2nd control stage.

pH and alkalinity, were controlled in the 2nd control stage after the BAC filtration process. Chemicals, such as Na_2CO_3 and CO_2, were injected to attain the target values. The amount of Na_2CO_3 injected ranged from about 6.64 L/day to 11.35 L/day (mean 8.51 L/day). CO_2 was not injected during the test.

Fig. 5(c) shows the result of pH control according to the control strategy in the 2nd control stage. The data were collected by on-line automatic measuring and analysis instruments installed in the AWTPP. The pH of the BAC effluent (pH 3) ranged from 6.95 to 7.50 (mean 7.16). In Korea, the pH standard for drinking water is 6.5-8.5. Because the target pH (demanded pH, DEpH2) should be lower than 8.5, the DEpH2 was set up at 8.2 and operated for an experiment period. The controlled water pH (pH4) after the 2nd control tank ranged from 8.07 to 8.54 (mean 8.37). The error range for DEpH2 8.2 was 0.0-0.084 (mean 0.023), which was only computed in relation to the pH.

Fig. 5(d) shows the result of alkalinity control according to the control strategy in the 2nd control stage. The BAC effluent alkalinity (Alk.2) before the 2nd control tank ranged from 51.39 mg/L as $CaCO_3$ to 66.04 mg/L as $CaCO_3$ (mean 57.13 mg/L as $CaCO_3$). The target alkalinity (demanded alkalinity, DEAlk.2) was set up and operated between 66 and 68 mg/L as $CaCO_3$ during the experiment period. The result for the controlled water alkalinity (Alk.3) after the 2nd control tank ranged from 63.98 mg/L as $CaCO_3$ to 76.10 mg/L as $CaCO_3$ (mean 69.86 mg/L as $CaCO_3$). The error range for DEAlk.2 was 0.0-0.107 (mean 0.04), which was only computed from the alkalinity. Over the operating periods, Alk.2 was lower than DEAlk.2; therefore, Na_2CO_3 was injected by the developed corrosion control system due to the difference in DEAlk.2 and Alk.2.

5. The Variation of CCPP and LSI for Final Treated Water

The CCPP concentration of the final treated water was controlled by the control strategy in each control step, with the important water factors adjusted to the target values. The LSI was additionally calculated by using the controlled water quality factors. Fig. 6 shows the CCPP concentration and LSI for the BAC effluent and

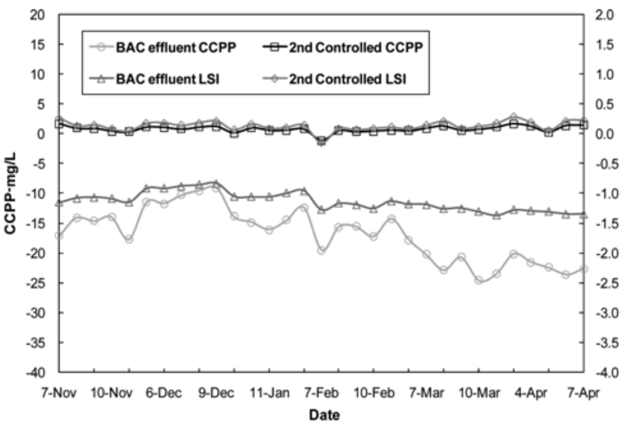

Fig. 6. The variations in the CCPP and LSI due to the corrosion control system.

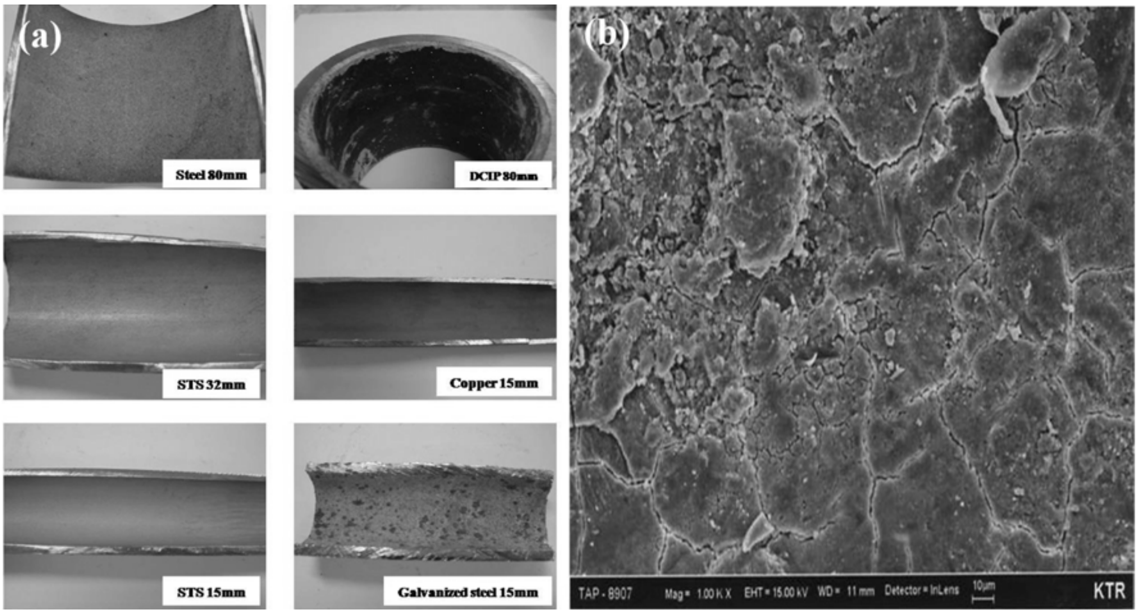

Fig. 7. The analysis of the inner surface of the simulated water distribution system (SWDS): (a) photographs as observed by the naked eye and (b) scanning electron microscope (SEM) photograph of a steel pipe (80 mm) after the corrosion test (magnification ~1,000×).

the finally controlled water after the 2nd control tank. The 2nd controlled CCPP concentration was collected by the corrosion control system, which was automatically calculated by the installed software in the control system. However, the CCPP concentration of the BAC effluent was computed only using the data collected from the instruments to gain an understanding of the difference in the variation of the CCPP between the controlled and uncontrolled water; therefore, the CCPP and LSI were calculated from the Rothberg, Tamburini & Winser (RTW) model ver. 3.0 [21]. From the result of the corrosive water control, the 2nd controlled CCPP ranged from −1.13 mg/L to 1.64 mg/L (mean 0.76 mg/L) and the LSI ranged from −0.16 to 0.28 (mean 0.13). The CCPP of the BAC effluent ranged from −24.65 mg/L to −9.13 mg/L (mean −16.90 mg/L), and the LSI ranged from −1.37 to −0.83 (mean −1.14). The results from this study show that compared to the LSI, CCPP control is more useful, not only qualitatively, but quantitatively also.

6. The Formation of Calcium Carbonate Films Caused by CCPP Control

To check the formation of corrosion products for the CCPP control greater than 0.0 mg/L, the inner surface of SWDS was analyzed by the naked eye (Fig. 7(a)). The stainless steel (STS diameter 15 mm and 32 mm) and copper (diameter 15 mm) pipes only varied slightly from the early state of the inner surface of the pipes. For the ductile cast iron pipe (DCIP, diameter 80 mm), the corrosion was slight, with only cracks and stripping phenomenon in the coated parts. Therefore, the STS, copper and DCIP pipe samples were excluded from the research pertaining to corrosion products. However, the corrosion products formed on the inner surface of the steel (diameter 80 mm) and galvanized steel pipes (diameter 15 mm) could be observed with the naked eye. The small light yellow granules were strongly adhered and evenly distributed on the inner surface of the steel pipe. The velocity of water in the steel pipe was maintained at 2.5 m/sec, but in the galvanized steel pipe, the granules were bigger and unevenly adhered to the inner surface as the

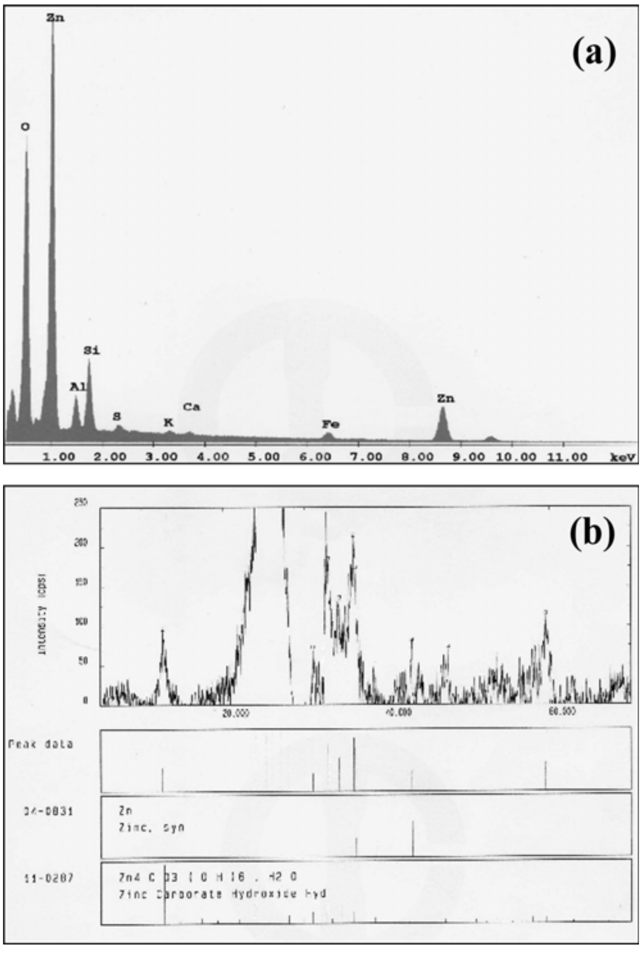

Fig. 8. (a) Energy dispersive X-ray spectroscopy (EDX) of the surface of an 80 mm steel pipe after corrosion control and (b) X-ray diffraction (XRD) of the corrosion products formed on an 80 mm steel pipe.

Table 6. The chemical composition of the inner surface via EDX analysis

Element	Weight %	Atomic %	K-ratio
Al	4.89	9.66	0.0228
Si	10.03	19.05	0.0608
S	0.92	1.53	0.0073
K	0.48	0.66	0.0046
Ca	0.52	0.70	0.0053
Fe	3.99	3.81	0.0436
Zn	79.17	64.59	0.7645

velocity was slower than in the steel pipe. The formed granules were strongly attached to the surface. The formation of calcium carbonate films due to the CCPP control were significantly different than those of the metallic oxide produced by corrosion.

Fig. 7(b) shows the SEM photograph of the inner surface of the steel pipe (80 mm) for the investigation of the surface structure. The SEM images show that the structures have boundaries for each particle, with the carbonate compound having several different sized crystals.

The chemical compositions of the crystals contained O, Al, Si, S, K, Ca, Fe, and Zn, with Zn and O found to be the major components (Fig. 8(a)). The data presented in Table 6 shows the elemental composition of the inner layer analyzed by EDX. Fig. 8(b) shows the result of the XRD spectrum of the corrosion products conducted on an 80 mm steel pipe. The crystalloid structure of the scale produced due to CCPP control in the inner surface of the pipe was zinc carbonate hydroxide hydrate ($Zn_4CO_3(OH)_6{\cdot}H_2O$). One of the strongly cohered carbonate compounds, $Zn_4CO_3(OH)_6{\cdot}H_2O$, can decrease the corrosion, with the role of overcoating the film formed on the inner surface of the pipe.

CONCLUSION

The characteristics of raw water show considerable fluctuation, but the characteristics of the advanced water treatment from a BAC process showed comparatively few fluctuations. However, the BAC effluent water was corrosive because the mean CCPP and LSI values of the BAC effluent were −16.9 mg/L and −1.14, respectively, which are quite low.

The DOC concentration of the effluent in the sand filtration and BAC process for advanced water treatment were 2.0 mg/L and 1.2 mg/L, respectively. Because the DOC concentration of the BAC process was decreased, the characteristics of the corrosive water were also increased.

The CCPP control system installed and operated according to the developed algorithm can maintain the CCPP condition range needed for corrosion prevention of water distribution system even if the BAC effluent contains strongly corrosive water.

The CCPP range of 0-4 mg/L was reasonably controlled for the induction of the formation of $CaCO_3$ film on the surface of the SWDS. The CCPP and LSI ranged from −1.13 mg/L to 1.64 mg/L (mean 0.76 mg/L) and from −0.16 to 0.28 (mean 0.13). The $CaCO_3$ films formed due to CCPP control were significantly different from the metallic oxide produced by corrosion. The crystalloid structure of the scale produced due to CCPP control in the inner surface of the pipe was zinc carbonate hydroxide hydrate ($Zn_4CO_3(OH)_6{\cdot}H_2O$), which can prevent the corrosion in metal pipes, with the role of overcoating the film formed on the inner surface of the pipe.

ACKNOWLEDGMENTS

This study was financially supported by the Eco-project of the Korea Institute of Environmental Science and Technology (Project No. 062-041-011), which was greatly appreciated.

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