

# Use of Hydrazine for Pitting Corrosion Inhibition of Copper Sprinkler Tubes: Reaction of Hydrazine with Corrosion By-Products

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The feasibility of using hydrazine for inhibiting pitting corrosion in copper sprinkler tubes was investigated by examining microscopical and structural evolution of corrosion by-products with SEM, EDS, and XRD. Hydrazine removed dissolved oxygen and reduced CuO and Cu<sub>2</sub>O as well. The stable phase was changed from CuO to Cu<sub>2</sub>O or Cu depending on hydrazine concentration. Hydrazine concentration of 500 ppm could convert all CuO corrosion by-products to Cu<sub>2</sub>O. In a tightly sealed acrylic tube filled with aqueous solution of 500 ppm hydrazine, octahedral Cu<sub>2</sub>O particles were formed while plate-like structures with high concentration of Cu, O, N and C were formed near a corrosion pit. The inside structure of a corrosion pit was not altered by hydrazine aqueous solution. Uniform corrosion of copper was almost completely stopped in aqueous solution of 500 ppm hydrazine. Corrosion potential of a copper plate was linearly dependent on *log* (hydrazine concentration). The concept of stopping pitting corrosion reaction by suppressing oxygen reduction reaction could be verified by applying this method to a reasonable number of real sprinkler systems before full-scale application.

**Keywords:** pitting corrosion inhibition, hydrazine, SEM, EDS, XRD

## 1. Introduction

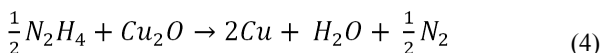
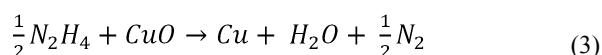
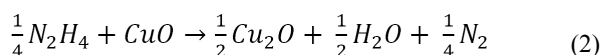
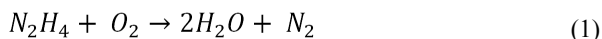
A significant number of wet sprinkler systems of the apartment buildings constructed from 2009 to 2014 in Korea have suffered severely from water leakage because of pitting corrosion in their copper tubing. Lee *et al.* [1] insisted that the carbon film formed on the copper tube caused the pinhole failure in the tube. They proposed removing carbon film as well as using phosphate or silica for preventing pitting corrosion of copper tubes. On the other hand, Suh *et al.* [2] and Kim [3] identified the pressurized air and sediments in the copper tube triggering the oxygen concentration cell corrosion as the cause of the pitting corrosion failure of copper tubes. Suh *et al.* [2] suggested that in order to inhibit water leakage by pitting corrosion of copper tubes in the already installed wet sprinkler systems, air should be almost completely removed from the copper tubing, and furthermore dissolved oxygen (DO) in the water should be reduced to such a low value that any existing oxygen concentration

cell stops functioning.

There are several ways of reducing DO in water [4]. Nitrogen bubbling and vacuum degassing belong to physicochemical methods while using chemicals such as hydrazine (N<sub>2</sub>H<sub>4</sub> or N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O: hydrazine monohydrate) or sodium sulfite (Na<sub>2</sub>SO<sub>3</sub>) to remove dissolved oxygen are chemical methods. By physicochemical method, DO smaller than 0.5 ppm can be attained while ppb level DO can be attained by chemical methods. Many times, physicochemical and chemical methods are used jointly to effectively reduce DO. To inhibit corrosion of a boiler made of steel, two to five times the hydrazine or sodium sulfite concentration equivalent to the dissolved oxygen concentration are used to maintain a low DO level in water [5]. However, it is hard to find cases of using either hydrazine or sodium sulfite to inhibit corrosion of copper tubes, particularly for inhibiting pitting corrosion of copper tubes in the wet sprinkler systems. The inner surface of copper tubes in the wet sprinkler systems is covered with a relatively thick layer of CuO and CuO<sub>2</sub>. This passive layer is supposed to inhibit both general and pitting corrosion of copper. This layer was not formed uniformly in the

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failed copper tubes of the wet sprinkler system, making the uncovered copper area vulnerable to pitting corrosion caused by the pressurized air remaining in the tubes. To determine the optimum concentration of hydrazine for reducing the DO level, it is necessary to consider carefully all the possible reactions of hydrazine ( $N_2H_4$ ) with  $CuO$  and  $Cu_2O$  covering the inner surface of the copper tube as well as with  $O_2$  dissolved in water. Equations (1) through (4) show the list of those reactions.



Much larger amount of hydrazine than needed to remove only dissolved oxygen should be used to inhibit pitting corrosion of copper tubes because hydrazine is consumed for reducing  $CuO$  as well. The reaction of hydrazine with the inside structure of the sprinkler copper tubes could be more complicated than the above simplified model, especially because nitrogen gas generated by the reaction of hydrazine with dissolved oxygen  $O_2$ ,  $CuO$  and  $Cu_2O$  may react with corrosion by-products in turn.

In this study, the authors investigated the reaction of hydrazine with the inner structure of the failed sprinkler copper tubes which suffered from water leakage, using different hydrazine concentrations, and tried to obtain important information such as the optimum hydrazine concentration for inhibiting pitting corrosion of copper tubes in the wet sprinkler system.



**Fig. 1** Inner surface of a failed copper sprinkler tube with mounds of corrosion by-products formed near the water-air line.

## 2. Experimental Procedures

### 2.1 Specimens for the test

Copper tubes removed from an apartment fire sprinkler system due to water leakage were used for the test. Small specimens of 8 mm x 8 mm cut from the copper tubes were used to study the effect of the hydrazine concentration on the reaction of hydrazine with the corrosion by-products. Copper tubes cut in halves were used to study the reaction of hydrazine in the tightly sealed acrylic tube.

### 2.2 Microscopical and structural characterization

Scanning electron microscopy (SEM) of a FEI Inspect F50 system was used to observe the surface morphology. An energy dispersive spectroscopy (EDS) attached on the SEM was used to analyze the composition of the inner surface of the copper tubes. The acceleration voltage of 20 kV was used for the SEM and EDS analyses. X-ray diffraction (XRD) spectra were obtained to differentiate the phases on the surface of the copper tubes, using a D/MAX-2500 diffractometer. XRD spectra were obtained in the two-theta range of 20 to 80 degree, using  $Cu K\alpha$  radiation at 40 kV and 200 mA.

### 2.3 Potentiodynamic test

The potentiodynamic tests were carried out to measure the corrosion properties of Cu in the aqueous solutions of different hydrazine concentrations. The opening of the Cu working electrode has a dimension of 1cm x 1cm. A saturated calomel electrode and a Pt plate were used as the reference electrode and the counter electrode, respectively. WonATech's WPG100 Potentiostat and Smart Interface were used for the measurement.

## 3. Results and discussion

### 3.1 Structural evolution of the corrosion by-products of copper sprinkler specimens by hydrazine treatment with different concentrations

Fig. 1 shows the inner surface of a copper sprinkler tube which suffered from water leakage due to pitting corrosion. There are three big mounds of corrosion by-products observed just below a white line which looks like a boundary between the water immersed area and the pressurized air area, suggesting that the waterline corrosion should be blamed for pitting corrosion failure of this sprinkler tube. The water immersed area has a black color, indicative of formation of a  $CuO/CuO_2$  layer.

Fig. 2a-d show the SEM images of the as-cut specimen of a failed copper sprinkler tube and the specimens (size:

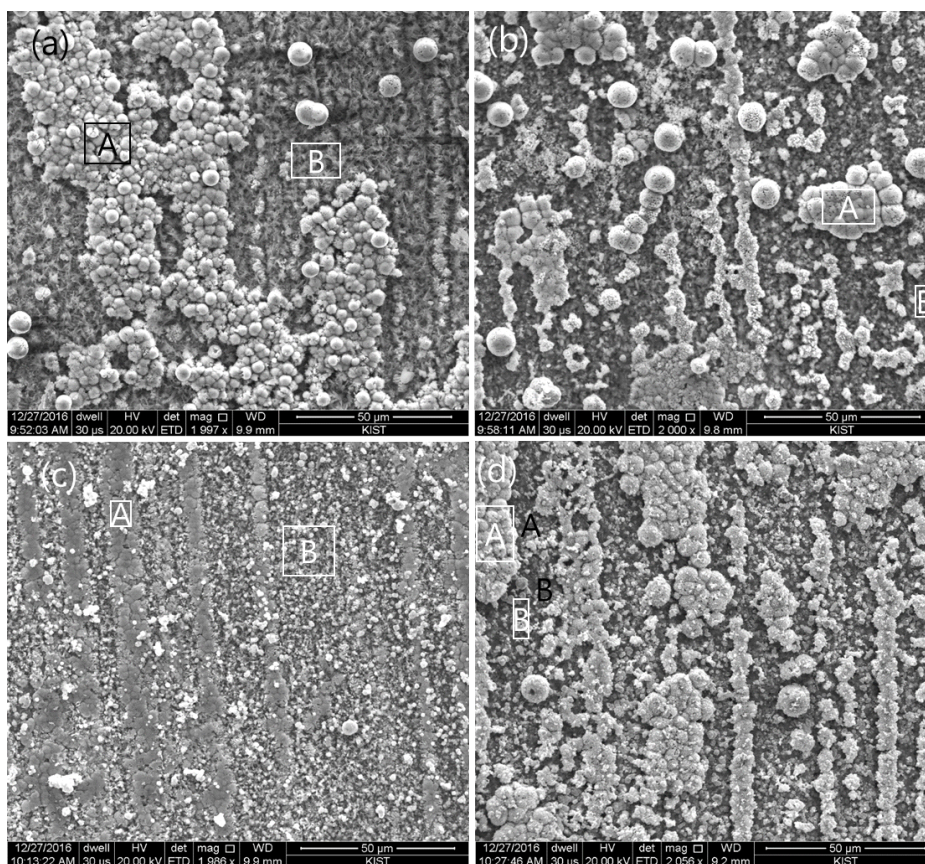


Fig. 2 SEM images of (a) the as-cut specimen of a failed copper sprinkler tube, and the specimens immersed for 6 days in aqueous solutions of hydrazine monohydrate concentrations of (b) 50 ppm, (c) 500 ppm, and (d) 5000 ppm.

Table 1 EDS analysis results of the as-cut specimen and the specimens immersed in aqueous solutions of different hydrazine concentrations (at%)

Specimen	As-cut		50 ppm		500 ppm		5000 ppm	
	A	B	A	B	A	B	A	B
CuK	56	61	54	59	73	61	93	75
OK	41	32	44	37	26	33	6	19
SiK	3	7	2	4	1	6	1	5

8 mm x 8 mm) which were cut from the same tube and immersed for 6 days in aqueous solutions of increasing hydrazine monohydrate (called here as hydrazine for simplification) concentrations of 50, 500, and 5000 ppm, respectively. Table 1 shows the EDS analysis results of the as-cut specimen and the specimens immersed in aqueous solutions of different hydrazine concentrations.

Fig. 3a-d show the XRD spectra of these specimens. There are two kinds of materials observed in the as-cut specimen: spherical particles gathered together forming bands (the area A) and the black base layer (the area B) with a feather-like structure. The spherical particles seem to be formed in the later stage of service of the sprinkler system and attached on the black base layer which were

formed in the early stage of service. The area A's composition is in the middle of CuO and Cu<sub>2</sub>O. The base layer B's composition corresponds to Cu<sub>2</sub>O with a high Si composition from 3 to 7 at%. Sand particles (SiO<sub>2</sub>) might have entered the copper tubing with water during installation, causing pitting corrosion. The XRD spectrum of this specimen (Fig. 3a) also shows that the surface consists of CuO and Cu<sub>2</sub>O.

The EDS analysis result of the specimen immersed in the 50 ppm hydrazine aqueous solution shows that the compositions of the base layer (the area B) and the spherical particles (the area A) have not changed much. The XRD spectrum of this specimen (Fig. 3b) also is not very much different from that of the as-cut specimen. When

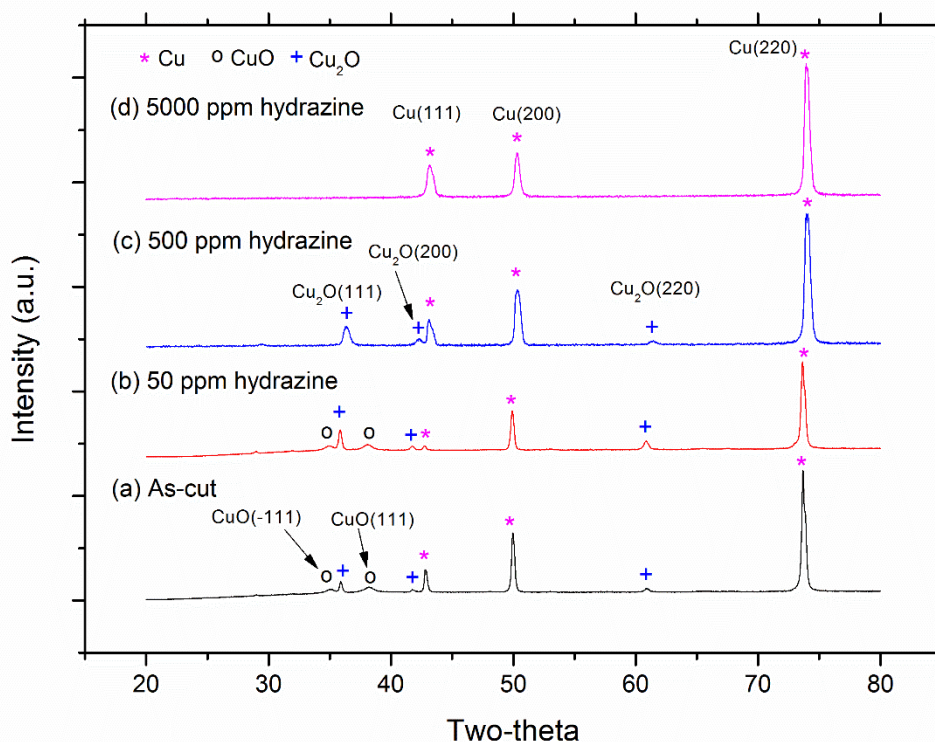


Fig. 3 XRD spectra of (a) the as-cut specimen of a failed copper sprinkler tube, and the specimens immersed for 6 days in aqueous solutions of hydrazine monohydrate concentrations of (b) 50 ppm, (c) 500 ppm, and (d) 5000 ppm.

the hydrazine composition was increased to 500 ppm, the area A which used to consist of spherical particles in the as-cut specimen became flattened, forming bands of Cu<sub>2</sub>O composition. It seems that when CuO was reduced to Cu<sub>2</sub>O by hydrazine, oxygen atoms were expelled from the structure, forming bands of Cu<sub>2</sub>O. On the other hand, the base layer is maintaining the Cu<sub>2</sub>O composition. The XRD spectrum of this specimen (Fig. 3c) consists of only Cu and Cu<sub>2</sub>O peaks, indicative of complete reduction of CuO to Cu<sub>2</sub>O.

When the hydrazine composition was increased to 5000 ppm, the morphology becomes very similar to what was obtained with the 50 ppm hydrazine concentration. There are bands of congregating spherical particles still remaining. However, the spherical particles have the completely different composition of almost Cu. Most of the base layer was also changed to Cu. The XRD spectrum of this specimen (Fig. 3d) shows only peaks of Cu, confirming almost complete reduction of CuO and Cu<sub>2</sub>O to Cu.

### 3.2. Structural change of the corrosion by-products of a failed copper sprinkler tube in a tightly sealed acryl tube.

A significant amount of nitrogen gas is generated when hydrazine reacts with CuO and Cu<sub>2</sub>O according to equations (2), (3), and (4). Fig. 4 demonstrates visually gen-

eration of nitrogen gas from a failed copper sprinkler specimen immersed in an aqueous solution of 500 ppm hydrazine in a 100 ml plastic bottle. The side of the bottle was left on the table so that water might leak through the cap when the pressure builds up inside the bottle. This is a kind of semi-open system because the cap cannot completely inhibit water leakage caused by the pressure build-up. The reaction started immediately and lasted for more than 7 days. The volume of nitrogen gas generated depends on the inner surface area of the specimen and

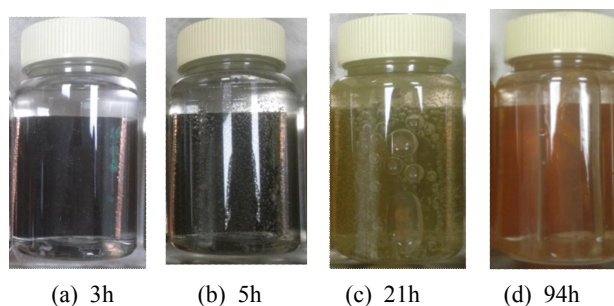


Fig. 4 Visual demonstration of nitrogen gas generation from a failed copper sprinkler specimen immersed in an aqueous solution of 500 ppm hydrazine in a 100 ml plastic bottle: (a) 3 hours, (b) 5 hours, (c) 21 hours, and (d) 94 hours after start of the experiment.



**Fig. 5** A closed model system made of an acryl tube and brass fittings for performing experiment of hydrazine reaction and corrosion inhibition. Notice the brightness of the tube surface and edge even after 10 months of experiment.

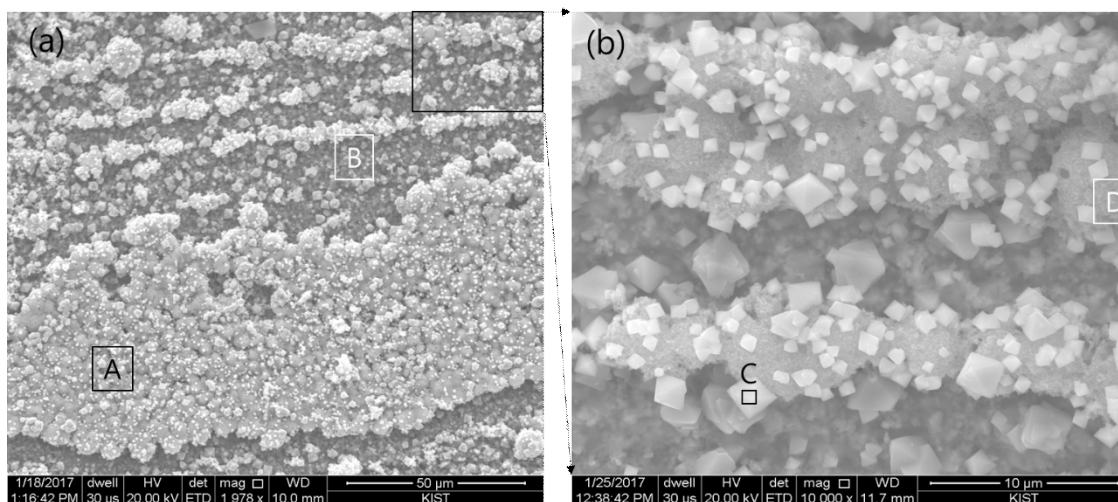
CuO thickness. For this experimental condition, the final volume of nitrogen gas was approximately 5% of the bottle. It should be also noticed that the black color of the inner surface of the specimen was changed to the brown color due to transformation of CuO to Cu<sub>2</sub>O. If this reaction continues in a closed system such as the wet sprinkler system, nitrogen gas generated will increase the pressure in the tubing. If the sprinkler water is pressurized for operation before the reaction of hydrazine with the corrosion by-products is completed, the pressure may rise to higher than 2 MPa, which may lead to rupture of copper tubing. Therefore, the pressure build-up in the tubing during the hydrazine reaction should be carefully managed in order to use hydrazine in the sprinkler system.

Under the atmosphere of a nitrogen gas of around 0.4 Mpa which was observed in a tightly closed tube filled with hydrazine aqueous solution and a copper sprinkler tube specimen, the hydrazine reaction might be different from what was observed in the last section where the nitrogen gas generated was minimal and the pressure build-up

was negligible due to the small size of the specimen and some leakage of water through the bottle cap.

In order to study the phenomena occurring in the aqueous solution of hydrazine and on the surface of the copper tubing and see whether corrosion of the copper sprinkler tube can be inhibited by the hydrazine treatment, a model system made of an acryl tube and brass fittings were designed (Fig. 5). After two halves of a failed sprinkler tube specimen were inserted into the acryl tube, hydrazine aqueous solution of 500 ppm was filled into the acryl tube up to the valve inlet and the valve was closed so that no air entered the acryl tube. The pressure inside the acryl tube went up to a highest gauge pressure of 0.4 MPa two days later and then slowly came down to 0.05 MPa after 10 months due to small leakage through the fittings. It should be noticed that the outer surface and the sawing cross section of the copper tube remains bright even after this long time of experiment, indicative of the very low level of dissolved oxygen inside the acryl tube and the effectiveness of hydrazine in inhibiting uniform corrosion.

Another experiment in the acryl tube with the same experimental conditions as the above continued for 15 days and the copper tubing was taken out and examined by SEM and EDS. The dissolved oxygen concentration of the water in the acryl tube was too low to be measured by the DO meter. Fig. 6 and Table 2 are the SEM images and EDS results, respectively, of an area a few centimeters away from a corrosion pit. Both the areas A and B in Fig. 6 have the composition of Cu<sub>2</sub>O. As for the composition, a similar result was obtained in the semi-open system (see Fig. 2c and Table 1). However, the enlarged image



**Fig. 6** (a) SEM image of an area far from a corrosion pit on a copper sprinkler tube immersed for 15 days in an hydrazine aqueous solution in an acryl tube, (b) the enlarged SEM image of the rectangular area of (a).

**Table 2 EDS analysis results at the positions indicated in Fig. 6 for a copper sprinkler tube immersed for 15 days in an hydrazine aqueous solution in an acryl tube (at%)**

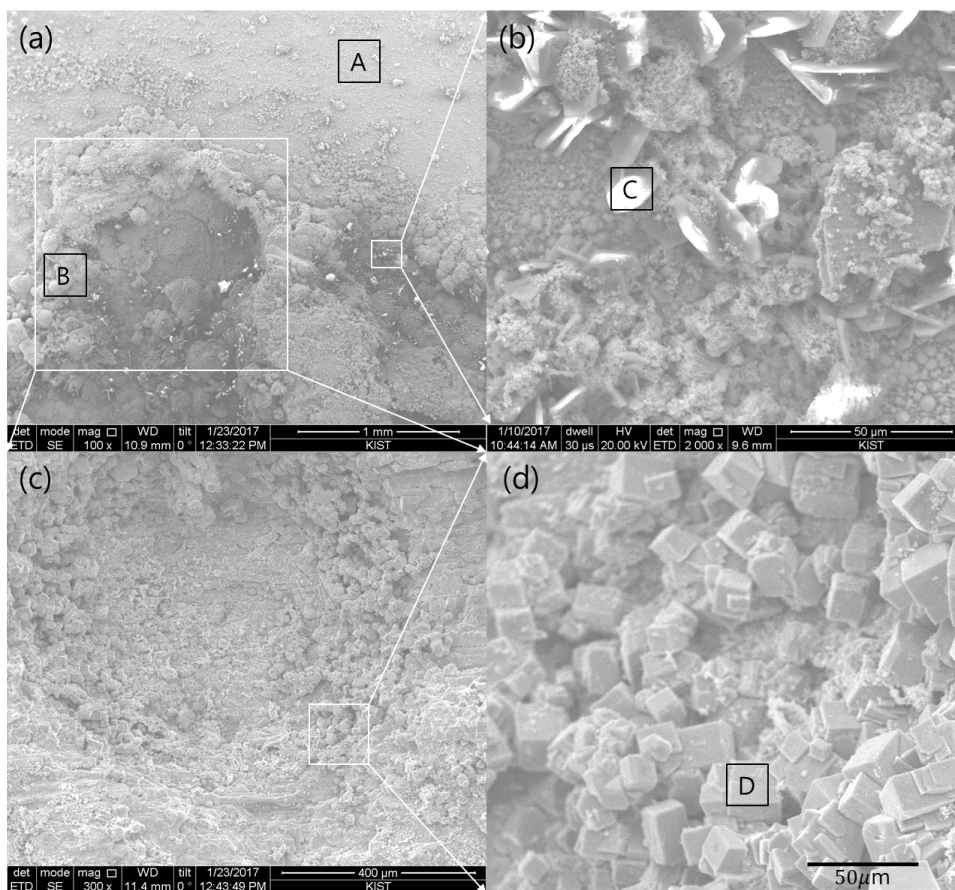
Position	A	B	C	D
Cu	69	63	65	92
O	29	32	34	7
Si	2	5	1	1

of this specimen shows a different and interesting morphology consisting of many octahedral particles sitting on a porous band structure. The octahedral particles were identified as  $\text{Cu}_2\text{O}$  crystallites by EDS. The porous band has a composition close to pure copper. It looks like that some of  $\text{CuO}$  materials on the bands were recrystallized as  $\text{Cu}_2\text{O}$  crystallites on top of the bands. It seems that somehow the high nitrogen concentration in the solution helped nucleation of octahedral  $\text{Cu}_2\text{O}$  crystallites

There is another interesting phenomenon observed near

a pitting corrosion area in the closed system. Fig. 7a shows a low magnification image of a corrosion pit. The flat area A has a  $\text{Cu}_2\text{O}$  composition while the bubble-shaped material B on the corrosion pit has a high concentration of carbon C, indicative of existence of the malachite [ $\text{Cu}_2(\text{OH})_2\text{CO}_3$ ] structure. It should be noticed that there are white plate-like structures around the corrosion pit. Fig. 7b is the high magnification image of one of those areas. Many plate-like structures are scattered in this area. One of those plates (the area C) was analyzed to contain high concentrations of Cu, O, N, and C. It is not clear how this plate-like structure was formed.

The cap of the corrosion pit was removed and the inside structure was examined by SEM and EDS. Fig. 7c and d are the low and high magnification images taken with the cap removed. The inside structure consists of cuboid  $\text{Cu}_2\text{O}$  particles (see Table 3 for the composition of the particle D), as usually observed in the corrosion pit of copper [2]. There is no change of the morphology, and



**Fig. 7 (a) low magnification SEM image of a corrosion pit without the cap removed, (b) high magnification SEM image of an area near the corrosion pit showing plate-like structures, (c) SEM image of the corrosion pit with the cap removed, and (d) high magnification SEM image of the square of the image (c). The specimen was immersed in an hydrazine aqueous solution of 500 ppm for 15 days in an acryl tube.**

**Table 3 EDS analysis results of the positions in Fig. 7 (at%)**

Position	A	B	C	D
Cu	70	48	40	76
O	28	45	21	24
C	-	7	16	-
N	-	-	23	-
Si	2	-	-	-

all the particles have flat surfaces without any evidence of chemical reaction. This result is expected because  $\text{Cu}_2\text{O}$  is the stable phase in the hydrazine aqueous solution of 500 ppm. It is concluded that the inside structure of the corrosion pit is not altered by hydrazine solution of this concentration even though there is a slight change of the outside structure of the corrosion pit.

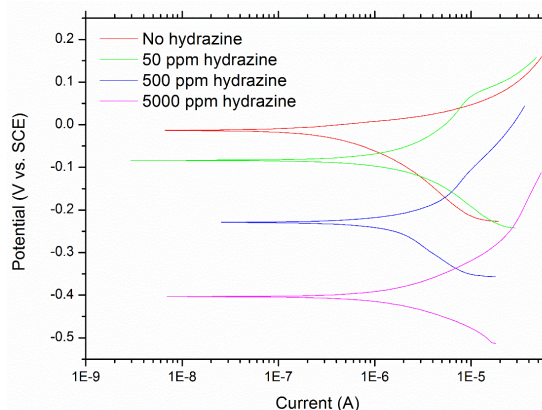
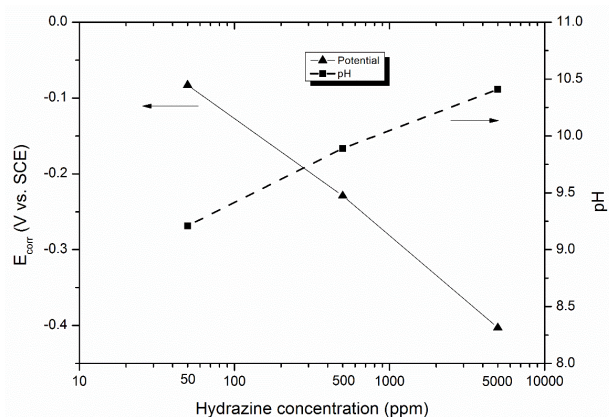
### 3.3. Results of the potentiodynamic polarization tests at different hydrazine concentrations.

As shown in section 3.1, when the hydrazine concentration is increased from 50 ppm to 500 ppm,  $\text{Cu}_2\text{O}$  phase instead of  $\text{CuO}$  phase becomes the stable phase. The stable phase is changed from  $\text{Cu}_2\text{O}$  to  $\text{Cu}$  as the hydrazine concentration is further increased to 5000 ppm. To understand the evolution of the stable phase with increasing hydrazine concentration, potentiodynamic polarization curves of a copper plate (Fig. 8) were obtained one day after aqueous solutions of different hydrazine concentrations were prepared, and the corrosion potential,  $E_{\text{corr}}$  obtained from the potentiodynamic polarization curves was plotted as a function of the hydrazine concentration in Fig. 9.  $E_{\text{corr}}$  decreases with  $\log$  (hydrazine concentration) almost with a linear dependence.

Since there are no appreciable amounts of  $\text{CuO}$  or  $\text{Cu}_2\text{O}$  formed on the  $\text{Cu}$  plate during the potentiodynamic experiment, hydrazine is consumed only to remove the dissolved oxygen in the water through the reaction of equation (1), and in that case the equilibrium concentration of dissolved oxygen is expected to be inversely proportional to the hydrazine concentration. As Fig. 9 shows, pH of the hydrazine solution also has a linear dependence on  $\log$  (hydrazine concentration). Therefore, the decrease of  $E_{\text{corr}}$  with hydrazine concentration should be the consequence of the decrease of dissolved oxygen and the increase of pH with increasing hydrazine concentration.

## 4. Discussion

Using the observation that the stable phase on the inner surface of the failed sprinkler copper tube is changed from

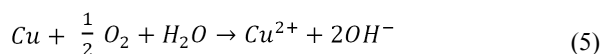

**Fig. 8 Potentiodynamic polarization curves of a copper plate obtained with the aqueous solutions of different hydrazine concentrations of 0, 50, 500, and 5000 ppm.**

**Fig. 9 Change of  $E_{\text{corr}}$  and pH with hydrazine concentration.**

$\text{CuO}$  and  $\text{Cu}_2\text{O}$ , to  $\text{Cu}$  with increasing hydrazine concentration and the pH values at different hydrazine concentrations, the potential and pH coordinates at the different hydrazine concentrations were roughly indicated on the Pourbaix diagram (potential-pH diagram) of the copper-water system (Fig. 10) [6]. The coordinate follows the yellow dotted line from  $\text{CuO}$  to  $\text{Cu}_2\text{O}$  and  $\text{Cu}$  stable regions as the hydrazine concentration increases.

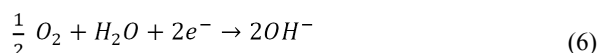
Yagi *et al.* [7] is the only group that performed the experiment similar to this study. They tried to control the oxidation state of  $\text{CuO}$  nanoparticles in a hydrazine aqueous solution by changing the temperature and pH of the solution. Their hydrazine concentration was  $0.50 \text{ mol dm}^{-3}$  corresponding to 25,000 ppm hydrazine monohydrate ( $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ ) solution, which is much higher than the compositions of this study. They observed conversion of  $\text{CuO}$  nanoparticles to a mixture of  $\text{Cu}$  and  $\text{Cu}_2\text{O}$  at pH 9.0 and 298 K, while complete conversion to  $\text{Cu}$  at pH 8.5 and 323 K and at pH 7.6 and 353 K was observed. Their

result that CuO is converted to Cu at a very high hydrazine concentration is the same as the result of this study. They could get only Cu at pH 9.0 and 298 K as well if an enough reaction time was allowed. Their reaction time was 2 h while our reaction time was 6 days.

The potential for inducing pitting corrosion can be obtained analytically as follows [2]. The corrosion reaction of Cu is given by equation (5).



This corrosion reaction consists of the half cell reaction at the cathode (equation (6)) and that at the anode (equation (7)).



The potential of the cathode reaction (6) which takes place at the high oxygen concentration region is given by equation (8) as a function of oxygen partial pressure  $p_{\text{O}_2}$  and  $pH$  at the cathode, which can be obtained from the Nernst equation.

$$E_{\text{cathode}} (\text{V}) = 1.23 + 0.015 \log P_{\text{O}_2} - 0.059 \text{pH} \quad (8)$$

Here, 1.23 V is the standard reaction potential of the cathode reaction (6).

The upper dotted line in the Pourbaix diagram Fig. 10 of the copper-water system is the plot of the cathode reaction potential when  $p_{\text{O}_2} = 1 \text{atm}$ . The potential of the anode reaction which takes place at the low oxygen concentration region such as inside a corrosion pit is given by equation (9).

$$E_{\text{anode}} (\text{V}) = -0.34 - 0.029 \log([\text{Cu}^{2+}]) \quad (9)$$

Here, 0.34 V is the standard reduction potential of Cu. The horizontal red line is the anode reaction potential when  $[\text{Cu}^{2+}] = 10^{-4} \text{M}$ . The potential  $\Delta E$  of the corrosion reaction of Cu (equation (5)) is the summation of equations (8) and (9).

$$\begin{aligned} \Delta E = & 0.89 + 0.015 \log P_{\text{O}_2} \\ & - 0.059 \text{pH} - 0.029 \log([\text{Cu}^{2+}]) \end{aligned} \quad (10)$$

The reaction potential  $\Delta E$  when  $p_{\text{O}_2} = 1 \text{atm}$ ,  $\text{pH} = 8$  and

$[\text{Cu}^{2+}] = 10^{-4} \text{M}$  is calculated as 0.53 V from equation (10). The reaction potential  $\Delta E$  which drives pitting corrosion can be obtained graphically as well from the Pourbaix diagram. The upward blue arrow line in Fig. 10 is the graphically obtained  $\Delta E$  with the same condition as above. It should be noticed that there is no difference between the analytically calculated potential  $\Delta E$  and the graphically obtained one.

If the state of water in terms of the potential and pH is located lower than the red line which is the boundary between Cu and  $\text{Cu}^{++}$  regions for the  $10^{-4}$  mole concentration of  $\text{Cu}^{++}$ , the pitting corrosion will not occur because of the negative potential for pitting corrosion. Therefore, if we reduce DO to such a low level that  $\text{Cu}_2\text{O}$  becomes the stable phase (the red circle in Fig. 10), pits will not be nucleated, and it is very possible that even the already existing pits will stop growing. To have such a state in which the DO concentration is very low, the hydrazine concentration should be high enough, i.e. around 500 ppm to transform all the CuO corrosion by-products into  $\text{Cu}_2\text{O}$ .

If the hydrazine concentration is very high such as 5000 ppm as in this study, the Cu phase becomes the stable phase because no driving potential is left for pitting corrosion. However, the problem is that all the CuO and  $\text{Cu}_2\text{O}$  phases are converted to Cu during the process, and nitrogen gas generated in each conversion process (see equations (3) and (4)) is two times the nitrogen gas generated during conversion of CuO to  $\text{Cu}_2\text{O}$  (equation (2)). Resultantly, hydrazine two to three times what is needed for converting to  $\text{Cu}_2\text{O}$  is needed. Another problem is that there is no passive layer  $\text{Cu}_2\text{O}$  left which might protect the bare Cu surface.

Based on the experimental results of this study, we conclude that the optimum hydrazine concentration should be high enough to convert all CuO phase to  $\text{Cu}_2\text{O}$ , but not so high as to convert CuO and  $\text{Cu}_2\text{O}$  phases to Cu [8]. Another important issue when using hydrazine as a chemical for inhibiting pitting corrosion is that nitrogen gas generated during the process should be carefully managed. Otherwise, the copper tube of the sprinkler system may rupture because of the high-pressure build-up by the nitrogen gas.

Our method assumes that if the oxygen reduction reaction, which is the cathodic reaction, is suppressed by reducing DO to a very low level, the anodic reaction inside the corrosion pit is stopped. However, it is well known that the water inside the already formed corrosion pit is acidic and it contains usually chlorine ions, which are two factors known to accelerate pitting corrosion once it is



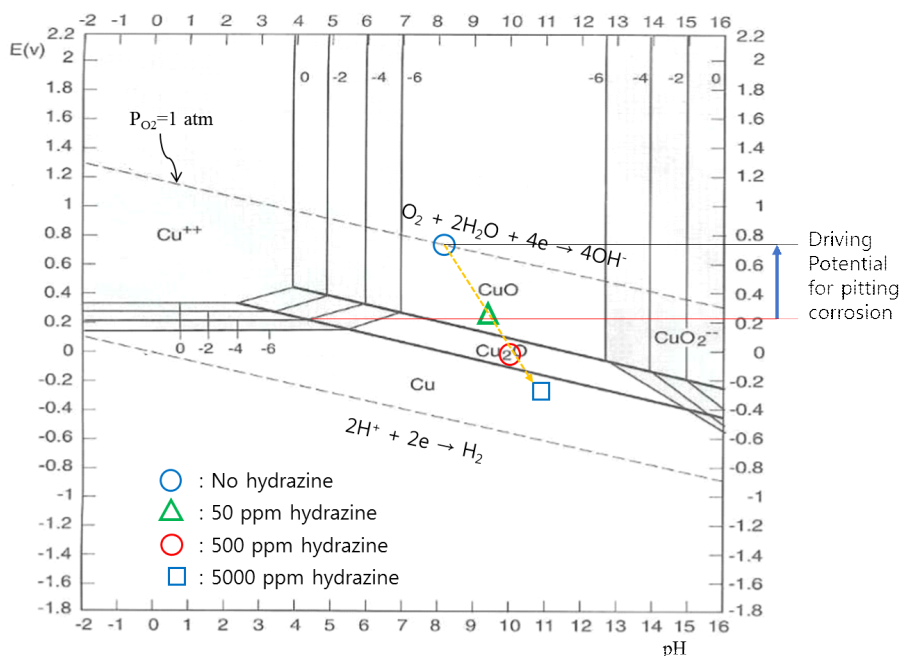


Fig. 10 Pourbaix equilibrium diagram of copper-water [6], showing the regions where each of  $\text{CuO}$ ,  $\text{Cu}_2\text{O}$ ,  $\text{Cu}^+$ , and  $\text{Cu}$  is the stable phase. 0, -2, -4, -6 represents base-10 log of ion activity. The states of the aqueous solutions of different hydrazine concentrations were drawn in the Pourbaix diagram.

formed [9-11]. Therefore, in order to confirm the feasibility of using hydrazine for inhibiting pitting corrosion in the wet sprinkler system, it would be necessary to test this method in a number of the real sprinkler systems and get meaningful statistical data on the occurrence of leakage.

## 5. Conclusions

1. The stable phase inside the copper sprinkler tube was changed from  $\text{CuO}$  to  $\text{Cu}_2\text{O}$  or  $\text{Cu}$  depending on the hydrazine concentration.
2. The hydrazine concentration of 500 ppm was high enough to convert all the  $\text{CuO}$  corrosion by-products to  $\text{Cu}_2\text{O}$  in addition to removing almost all dissolved oxygen.
3. In a tightly sealed acrylic tube filled with an aqueous solution of 500 ppm hydrazine, octahedral  $\text{Cu}_2\text{O}$  particles were formed while plate-like structures with high concentrations of  $\text{Cu}$ ,  $\text{O}$ ,  $\text{N}$ , and  $\text{C}$  were formed near a corrosion pit.
4. The inside structure of a corrosion pit was not altered by hydrazine aqueous solution.
5. The corrosion potential of copper was linearly dependent on  $\log$  (hydrazine concentration).
6. Hydrazine could be an effective chemical for removing dissolved oxygen for inhibiting both uniform and pit-

ting corrosion of copper tubing in the wet sprinkler. The idea of stopping pitting corrosion reactions by removing dissolved oxygen could be verified by applying this method to a reasonable number of real sprinkler systems before full-scale application.

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