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EXPERIMENTAL RESEARCH ON PC STEEL EMBRITTLEMENT

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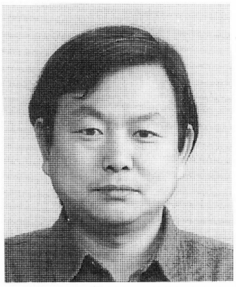
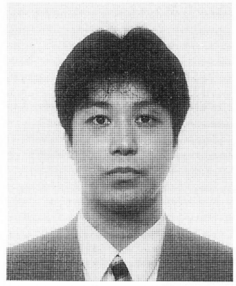

Kazuhiro IKAWA Naoyuki Sugihashi

This paper discusses the results of experiments on the hydrogen embrittlement of PC steel, which poses various problems when the cathodic protection method is applied to PC structures. The effects of cathodic polarization and environmental factors on hydrogen embrittlement are clarified, along with the effects of exposure period on stress, conditions of hydrogen evolution, and the possibility of recovering the mechanical properties after hydrogen embrittlement. Laboratory tests were carried out to assess the volume of hydrogen occluded in steel and the condition of specimens subjected to long-term exposure. Based on the findings of these experiments, the applicability of cathodic protection to PC structures is discussed.

Keywords: *Cathodic protection, hydrogen embrittlement, prestressing steel, recovery from hydrogen embrittlement, hydrogen thermal analysis*

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1. INTRODUCTION

In recent years, cathodic protection has attracted attention as a means to prevent salt damage and deterioration in concrete structures, and it has already been adopted in some cases on a trial basis. Under these circumstances, the applicability of cathodic protection to PC structures is now being discussed [1], with particular attention to the problem of hydrogen embrittlement of PC steel due to excessive cathodic current and to the current's uneven distribution. Although few structures have actually collapsed due to stress corrosion and hydrogen embrittlement [2,3], high-tensile steel such as PC steel is considered susceptible to hydrogen embrittlement. There have, however, been very few studies of this phenomenon, and most that have been reported were conducted in laboratories. Consequently, only a few published reports are available on PC steel in actual structures.

To assess the basic characteristics of PC steel hydrogen embrittlement and the environmental factors that affect this phenomenon, hydrogen-penetrated PC steel wires by cathodic polarization were prepared in laboratory tests, were observed the rupture surface by SEM. In addition, cathodic protection was applied to a specially manufactured PC beams and they were exposed to a marine environment. Sample steel wires were later extracted from the PC beams and tested to clarify whether hydrogen embrittlement had taken place. The possibility of recovery of mechanical properties after hydrogen embrittlement was also studied.

2. TEST METHOD

2.1 Outline of Tests

Laboratory tests were implemented, long-term exposure tests (by spraying sea water and simulating the conditions of hydrogen evolution), and verification tests with concrete specimens. In all cases, commercially available PC steel wires were used.

a)Laboratory tests
The test PC steel wires were cathodically polarized in an aqueous solution and slow-strain tensile test were implemented. The results of this test with those from a slow-strain tensile test (mechanical property test) in air were then compared with tests under cathodic poralization in order to evaluate the wires' susceptibility to hydrogen embrittlement. The rupture surface were also observed by SEM. The following factors were studied in the laboratory tests :
(1)Effect of the potential of cathodic polarization (series I)
(2)Effect of the exposure environment (pH, dissolved oxygen, chloride ions) (series II)
(3)Effect of exposure period on stress and conditions of hydrogen evolution (series III)
(4)Possibility of recovery from hydrogen embrittlement (series IV)
b)Verification tests on concrete specimens after long-term exposure
In the series V tests, sea water was sprayed on specially manufactured pretensioned beams over an extended period, applying cathodic polarization from external power sources up to the potential of hydrogen evolution for PC steel. After subjecting the beams to this long-term exposure tests, the sample PC steel wires were extracted from these and slow-strain tensile tests were conducted in the same manner as in the laboratory tests, in order to evaluate their susceptibility to hydrogen embrittlement and confirm whether such embrittlement had actually occurred. The volume of hydrogen occluded in the PC steel wires was also measured to discuss hydrogen's penetration and emission behavior.

2.2 Test Method

a) Specimens

In the series I to IV tests, specimens used were commercially available single wires with a diameter of 5 mm. The specimens were machined to a diameter of 4 mm for a length of 70 mm at the center, then polished with # 2400 emery and degreased with acetone. Other parts were wrapped with Teflon tape for electrical insulation. See Figure 1 for dimensions and a profile, and Tables 1 and 2 for their chemical composition and mechanical properties. In the series V test, specimens used were 7-wire strand with a diameter of 9 mm. After extracting the PC steel wires from the concrete beams, any attached concrete was removed and the wires were wrapped with Teflon tape for electrical insulation, except in the part to be tested. Specimens in this series were not machined, emery-polished, or degreased. See Tables 1 and 2 for their chemical composition and mechanical properties.

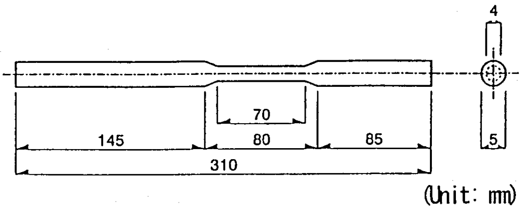


Figure 1 Profile and Dimensions of Specimen

Table 1 Chemical Composition of Specimen

Specimen	C	Si	Mn	P	S	Cu
φ5-Single Wire	0.82	0.19	0.53	0.012	0.006	0.030
7-Wire Strand	0.76	0.24	0.83	0.011	0.002	0.006

(Unit : WT%)

Table 2 Mechanical Properties of Specimen

Specimen	Tensile Strength (MPa)	Yield strength (MPa)	Elongation (%)
φ5-Single Wire	1762	1530	5.3
7-Wire Strand	1922	1844	5.4

b) Concrete beam specimen

In the series V test, specimens used were pretensioned PC beams 60 (W) x 60 (H) x 1,800 (L) made of high-early-strength portland cement at a water-cement mix ratio of 37.2%. The mixing water contained 15 kg/m^3 of NaCl. Table 3 shows the specific mix used. The effective prestress on the PC steel was about 50% of its tensile strength. In order to achieve a current flow through the PC steel wire, a mesh anodes were pasted, shown in Figure 2, onto the concrete surfaces and was coated with a cement-base repair material. To prevent any chloride invasion, the ends of the specimens were coated with an epoxy resin.

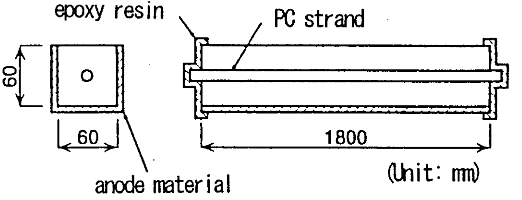


Figure 2 Profile and Dimensions of Concrete Specimen

Table 3 Spcific Mix

Gmax (mm)	W/C (%)	S/a (%)	Unit Volume (kg/m^3) W	C	S	G	AE	NaCl
20	37.2	41.0	160	430	737	1076	5.1	15

c) Cathodic polarization test

Cathodic polarization tests were performed to measure the potential for hydrogen evolution by filling the cell with a saturated $Ca(OH)_2$ aqueous solution to simulate concrete conditions, and using a zinc amalgam or platinum galvanized titanium wire as the anode and a mercury oxide or saturated calomel electrode as the reference electrode. In this test, the dissolved oxygen in the aqueous solution was removed by passing nitrogen through it. The potential of specimen was shifted cathodically at a speed of 20 mV/min.

d)Exposure of concrete specimen

After aging the concrete specimens for about three months, they were subjected to an exposure test with a duration of about 5.5 years. In this test, sea water was sprayed on the specimen (one period in the morning and once at night, for three hours each time) and the specimens were cathodically polarized up to the potential of hydrogen evolution using an external power source. Specimens for a non-current test were also installed. During this exposure test, the instant-off potential was regularly measured to judge whether the potential for hydrogen evolution was maintained.

e)Slow-strain tensile test

Tensile tests were conducted at a strain rate of about 1×10^{-6} in an aqueous solution. See Figure 4 for a schematic diagram of the test. To prevent the saturated $Ca(OH)_2$ aqueous solution in the cell from flowing out during the series V test, the cell was filled with in sponge. After the test, the specimen's elongation, yield (point) strength, tensile strength, rate of reduction in area, and rupture strength were measured. They were compared with the corresponding mechanical properties obtained from the slow-strain tensile test in air. The specimen's susceptibility to hydrogen embrittlement was evaluated based on the ratio of hydrogen embrittlement expressed by equation (1).

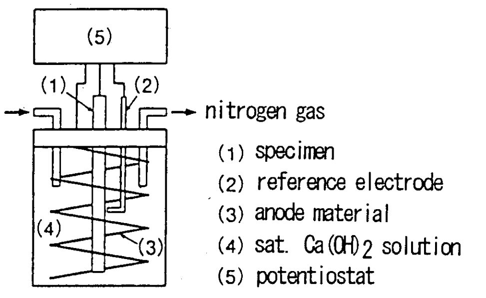


Figure 3 Schematic Diagram of Cathodic Poralization Test

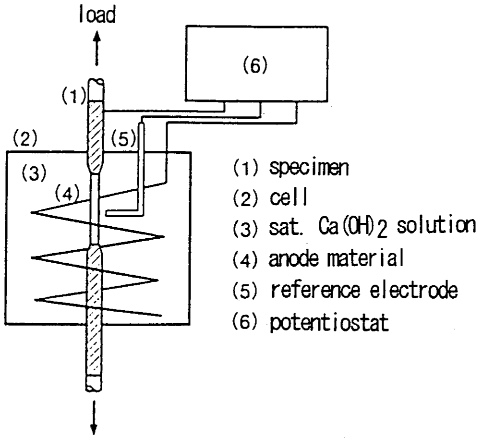


Figure 4 Schematic Diagram of Slow Strain Tensile Test

$$Ix = (Xair - Xcathod) / Xair \times 100 \qquad (1)$$

where

Iz	: ratio of hydrogen embrittlement (%)
X	: some mechanical property
air	: suffix denoting measurement in air
cathod	: suffix denoting measurement under cathodic polarization

Equation (1) indicates that a higher absolute value of hydrogen embrittlement ratio means a higher susceptibility to embrittlement. Properties are represented by the average value of three specimens in the test series I to IV, and of two or three specimens in test series V.

f)Hydrogen analysis of PC steel by vacuum heating

The volume of hydrogen occluded in the series V specimens as assessed immediately after the current flow was stopped and then at one, three, and seven days thereafter. The vacuum heating method was used[5]. The PC wire specimens were cut from the concrete beam and stored in a dry ice tub to prevent diffusion of hydrogen. Specimens were form the specimen after it had stood for one, three, and seven days. The specimens were heated in a vacuum at a rate of 200℃/h and the volume of discharged hydrogen was measured with a mass spectrometer. Curves of the volume of hydrogen discharged over the temperature range from room temperature to about 800℃

were then plotted, and the volumes emitted in three sub-divided temperature ranges measured and totalled.

3. Hydrogen Embrittlement and Hydrogen Evolution Potential

3.1 Mechanism of Hydrogen Penetration and Hydrogen Evolution Potentail

In the cathodic protection of steel in concrete, the reaction given by equation (2) is thought to take place on the steel surface when over-protection.

$$H_2O + e^- \rightarrow H(ad) + OH^- \quad \cdots\cdots (2)$$

where (ad): atom

Equation (2) describes the reaction of hydrogen atom formation, after which the following reaction takes place.

$$H(ad) + H(ad) \rightarrow H_2(ad) \quad \cdots\cdots (3)$$

$$H_2(ad) \rightarrow H_2(gas) \quad \cdots\cdots (4)$$

where (g): gas

This equilibrium potential (E_H) is expressed by (5) based on the Nernst's equation.[6]

$$E_H = -242 - 59pH \ (mV,\ SCE,\ 25℃) \quad \cdots\cdots (5)$$

The actual potential for hydrogen evolution is smaller by an amount equivalent to the over-voltage due to the reactions by equations (3) and (4).[6]

An outline of the mechanism by which hydrogen penetrates the steel is as follows.
(1) The H_2O on the steel surface decomposes as shown by (2) and the hydrogen atoms generated are adsorbed to the steel surface.
(2) There are two different processes which the adsorbed atoms follow. In one process, two atoms combine with each other to form hydrogen gas (H_2(gas)). In the other process, atoms penetrate the steel as single atoms.
(3) The atoms penetrate the steel and diffuse through the crystal lattice. They form hydrogen molecules by bonding with other atoms in places where trap sites, such as faults exist. The cause of hydrogen embrittlement is the adsorbed atoms, not the hydrogen gas. Therefore, the cathode polarization potential threshold for hydrogen embrittlement is near the equilibrium potential in (3). This paper regards this potential as the hydrogen embrittlement potential ; potential values have all been converted to a saturated calomel potential.

3.2 Environment and Potential Required Hydrogen Embrittlement

To estimate the conditions of hydrogen evolution, the Tafel range (within which the polarization curve can be taken as a straight line) was extrapolated to the equilibrium potential calculated from Nernst's equation for an aqueous solution of pH 12.5.

The PC steels in actual structures are subjected to stress. Figure 5 shows the results of an evaluation of the effect of loading stress, which was fixed at an allowable value of PC steel tensile stress[7] (60% of the tensile strength) to reflect the conditions found in actual structures. The exchange current density was about 0.01 $\mu A/cm^2$ irrespective of the load stress. It was found, therefore, that the conditions for hydrogen evolution in the elastic range include a current density of 0.01 $\mu A/cm^2$ or over and a potential lower than the equilibrium potential.

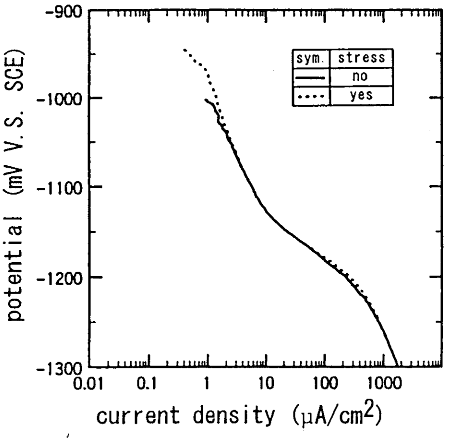


Figure 5 Cathodic Polarization Curve and Load Stress

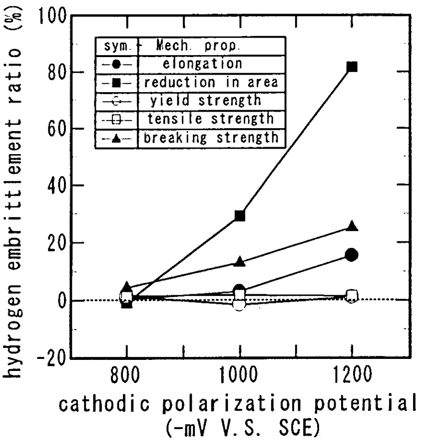


Figure 6 Effect of Polarization Potential (Series I)

The pH of neutralized concrete has been reported to be 8 to 10. In this case, the hydrogen evolution potential would be calculated as -710 to 830 mV, which is higher than that for ordinary concrete. This fact must be noted in protecting neutralized concrete structures.

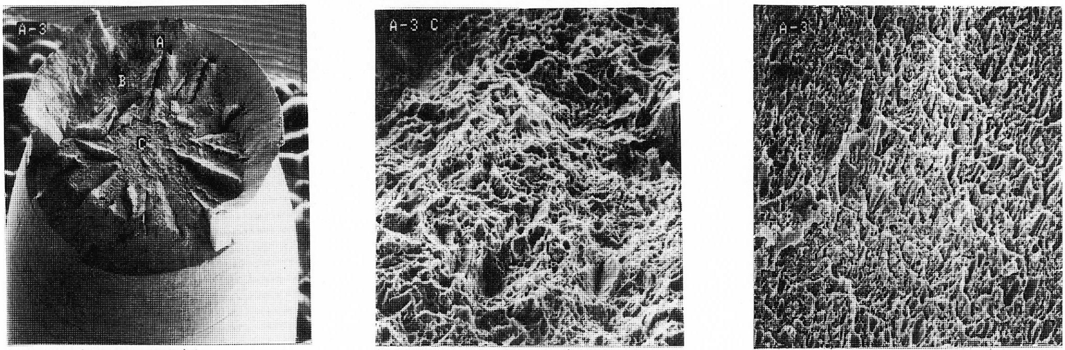
4. Environment and Susceptibility to Hydrogen Embrittlement

4.1 Effect of Polarizing Potential

In the series I test to investigate the cathodic polarization potential that causes hydrogen embrittlement, a saturated $Ca(OH)_2$ aqueous solution which was not deaerated was used. By taking into account the test results in 3.2, the polarizing potentials wre set at -800, -1,000, and -1,200 mV. Figure 6 shows the test results.

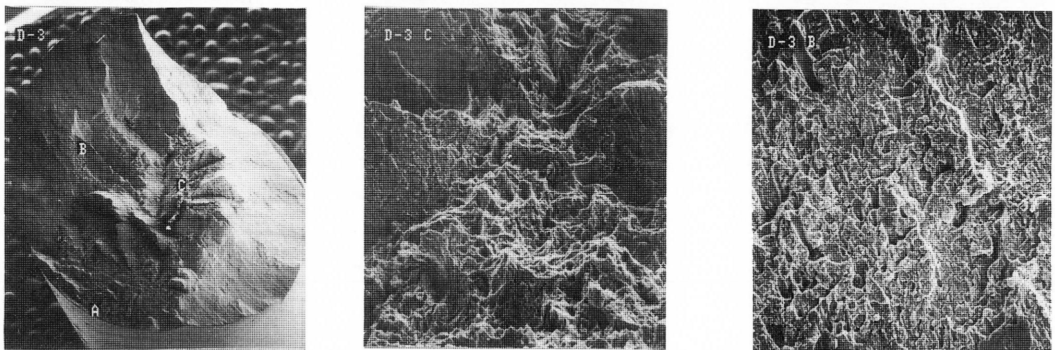
When the specimen is subjected to cathodic polarization at a potential lower than -1,000 mV, the relative susceptibility of the area reduction ratio, rupture strength, and elongation to hydrogen embrittlement tends to increase. However, there is no change in the susceptibility of tensile strength. The susceptibility of area reduction ratio is particularly notable. If it take into account that a previous report that the effect of hydrogen embrittlement on mechanical properties is most clearly seen in the area reduction ratio and the fact that the hydrogen evolution potential was -980 mV, it can be conclude that hydrogen embrittlement took place in this series of tests when the specimen was polarized at a potential lower than -1,000 mV.

Photos 1a) to 1c) show the surface fractography after rupturing in air as seen by SEM. Photos 2a) to 2c)show the surface fractography after rupturing under cathodic polarization at -1,200 mV. Macroscopically, the surface ruptured in air and not subjected to hydrogen embrittlement appears to have a cup and cone rupture morphology, as is clear in Photo 1a). The rupture morphology of the specimen under cathodic polarization at -1,200 mV and with apparent hydrogen embrittlement dose not observe reduced cross-sectional area, as seen in Photo 2a). As Photos 1b) and 2b) show, the central part of the rupture surface has a dimple rupture morphology indicative of ductile failure. Around the periphery, a similar dimple rupture morphology is seen in Photo 1c), and a flaky pseudo-cleavage plane in Photo 2c).



a)Mag. 25× b)Center, Mag. ×1000 c)Periphery, Mag. ×1000

Photo 1 Ductile Rupture Surface (Tested in Air)



a)Mag. 25× b)Center, Mag. ×1000 c)Periphery, Mag. ×1000

Photo 2 Embrittled Rupture Surface (Tested under Cathodic Polarization at -1200mV)

The pseudo-cleavage plane, which is reportedly a typical hydrogen embrittlement rupture plane[8], indicates that hydrogen embrittlement occurred in this case.

To investigate whether hydrogen embrittlement also occurs in the PC steel in actual structures, steel wire specimens cut from the no-current concrete beam specimens were tested. Figure 7 shows the test results, where the rate of reduction in area is represented by the rupture element line with the smallest rate of reduction. When the specimen experiences cathodic polarization at a potential lower than -1,000 mV, the effect of hydrogen embrittlement on area reduction ratio tends to increase, as in the data shown in Figure 6. However, the ratio of embrittlement itself is larger than that in Figure 6, presumably because of the difference in material (in terms of strength and composition).

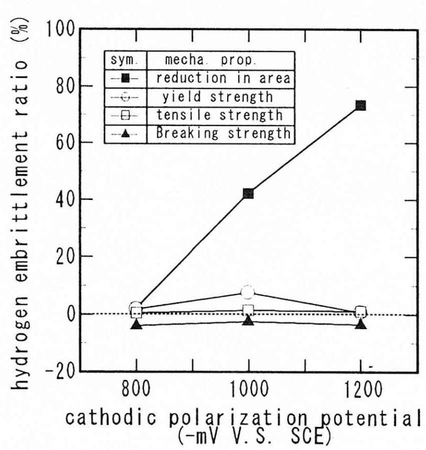


Figure 7 Effect of Polarization Potential (Series V)

These findings lead to the conclusion that PC steels in an actual structures is also subjected to hydrogen embrittlement, if subjected to cathodic polarization at a potential lower than that for hydrogen evolution, just as seen in the laboratory tests.

4.2 Effect of Environment

The concrete surrounding PC steel is not uniform, and the chloride ion concentration, humidity, and other factors vary by location. To investigate the effects of the environment surrounding the PC steel, therefore, the series II tests were implemented under varying conditions of the aqueous solution. These conditions were (1) amount of dissolved oxygen (saturated or deaerated), (2) chloride ion concentration (0, 3, or 5 %), and (3) pH (saturated $Ca(OH)_2$ aqueous solution or pure water). Figure 8 shows the relation between external conditions and the effect of hydrogen embrittlement on area reduction ratio. As this figure shows, the dissolved oxygen and chloride ion concentration had little effect. However, the ratio of hydrogen embrittlement is affected by pH, because of the higher potential for hydrogen evolution as described in 3.2. In applying cathodic protection to actual structures, therefore, it is important to pay attention to the carbonation of concrete around PC steel has environmental conditions affect.

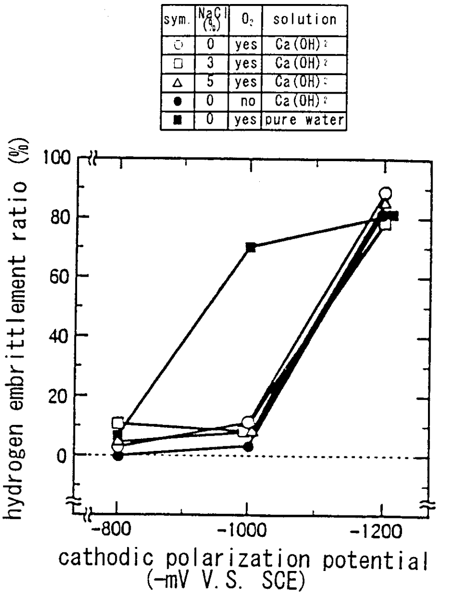


Figure 8 Effect of Environment

4.3 Effect of Exposure Period on Stress and Conditions of Hydrogen Evolution

The PC steels in actual structures are subjected to stress. If the frequency of inspections[1] once cathodic protection is implemented can be assured, over-protection at a potential less than -1,000 mV will, if it occurs, last no more than three months. Considering this, the series III tests were implemented by applying a stress measuring 60% of the tensile strength, to specimens and exposing them to conditions of hydrogen evolution for zero, one, and three months. Specimens were subjected to cathodic polarization in a saturated $Ca(OH)_2$ aqueous solution. During the test, stress and instant-off potential were measured once a week to keep the stress and to confirm that the desired potential of cathodic polarization was maintained.

Figure 9 shows the test results. When the specimen was polarized at -800 mV, which is above the potential of hydrogen evolution, there were no changes in the ratio of hydrogen embrittlement. At polarization voltages of -1,000 and -1,200 mV, some changes were seen in the ratio of hydrogen embrittlement, depending on the stress and period of exposure. At -1,000 mV, the ratio of hydrogen embrittlement fell as the specimen was exposed for longer periods to the conditions which cause hydrogen evolution. At -1,200 mV, this tendency was reversed but less conspicuous.

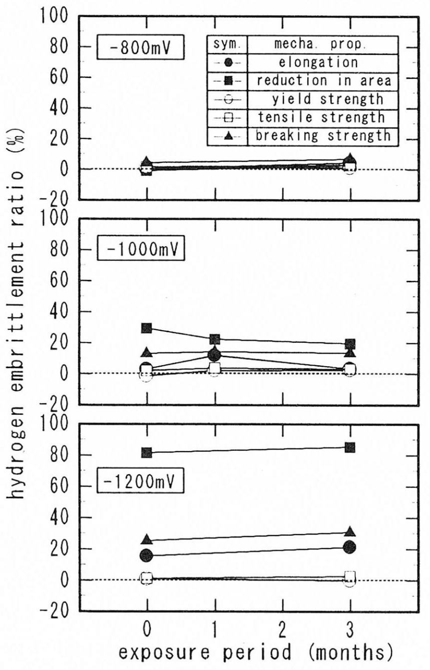


Figure 9 Effect of Exposure to Stress and Condition

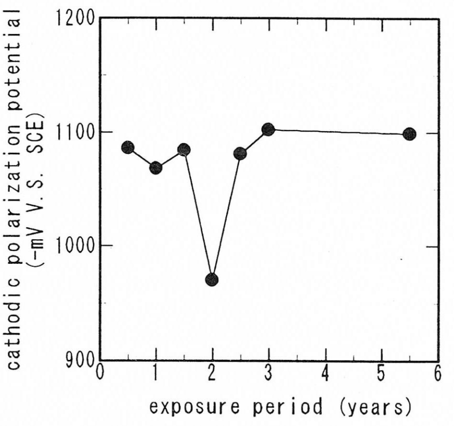


Figure 10 Transition of Instant-Off Potential

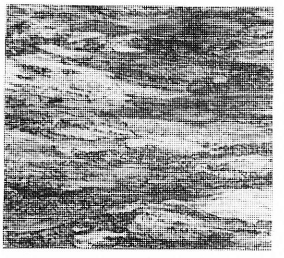


Photo 3 Fractgraphy of Specimen (7-Wire Strand, Axial Conditon)

Figure 10 shows the state of cathodic polarization of a specimen subjected to extended stress and current in concrete under conditions which cause hydrogen evolution. As shown in Figure 10, the PC steel was subjected to cathodic polarization at the potential of hydrogen evolution throughout the exposure period. Slow- strain tensile tests was implemented, using PC steel specimens cut from the concrete specimens immediately after the current flow was stopped; cathodic polarization was -1,000 mV. The test indicated that the effect of hydrogen embrittlement on area reduction ratio was 49%, a value slightly larger than that in the no-current test specimen (42%). Based on the results of the series III tests, it can be conclude that the ratio of hydrogen embrittlement increases as the specimen is exposed for longer periods to the conditions which cause hydrogen evolution.

Stress is thought to facilitate hydrogen embrittlement in two ways: (1) by cutting atomic bonds and (2) by increasing the material's capacity to absorb hydrogen due to plastic deformation. Yamakawa et al.[9] and Takai et al.[10] have reported that the content of hydrogen (in PC steel) increases as stress rises. However, their studies covered only the range above yield strain, and they also differed from the series V tests in terms of (1) type of steel and (2) stress in the elastic range. Consequently, a direct comparison with their findings is not possible. From a metallurgical viewpoint, however, both are related to the pearlite texture[11] in which cementite and ferrite exist as shown in Photo 3. According to D.I. Phalen[12] and other researchers, the volume of hydrogen occluded in ferrite does not increase based on either the presence or degree of stress. Taking these various results into considerration, it can be conclude that the load stress in the series III and V tests, which was in the elastic range, was not the cause of the increased ratio of hydrogen embrittlement.

Instead, the increase in the ratio of hydrogen embrittlement when the specimens experienced extended exposure to conditions which cause hydrogen evolution seems to have been caused by the increase in the amount of hydrogen occluded in the PC steel. This hypothesis is compatible with the finding that the ratio of hydrogen embrittlement rose when the volume of emitted hydrogen increased as the cathodic polarization voltage was lowered from -1,000 mV to -1,200 mV in 4. (1).

5. Possibility of Recovery from Hydrogen Embrittlement

Hydrogen embrittlement occurs when hydrogen penetrates steel. A number of theories have been proposed concerning the mechanism behind this phenomenon. Among these theories, there is currently a general agreement that hydrogen diffused into PC steel will cause cracks when trapped by microvoids and/or dislocations. If this diffused hydrogen can be removed, therefore, it show be possible to prevent hydrogen embrittlement and recover the properties of the PC steel. According to Suzuki et al.[13], steel bars containing occluded hydrogen emit diffused by eliminating trap sites when kept the temperature is high enough. Although it is not practical to keep actual structures at high temperatures, it is possible to cut the current flow temporarily and thereby avert the conditions which cause hydrogen evolution.

In the series IV tests, slow-strain tensile tests were implemented. Specimens had not been subjected to cathodic polarization, but had instead been subjected to a load stress and to conditions which cause hydrogen evolution for three months. One group of specimens were tested without cathodic protection immediately after stopping the current flow, and the other were tested without cathodic protection after keeping it loaded in an aqueous solution for seven days. The results were then compared with those in 4.3. Figure 11 shows the test results for series IV. The recovery period of zero days means that the test was conducted with cathodic polarization immediately after the current flow had stopped. Recovery periods of one and seven days mean these tests were conducted without polarization immediately after current flow had stopped and seven days after the end of cathodic polarization, respectively. As Figure 11 shows, the specimens polarized at -1,000 mV recovered their mechanical properties to the level in air after one day of recovery. Under cathodic polarization of -1,200 mV, however, one day of recovery was not sufficient. In this case, it took seven days for mechanical properties to fully recover.

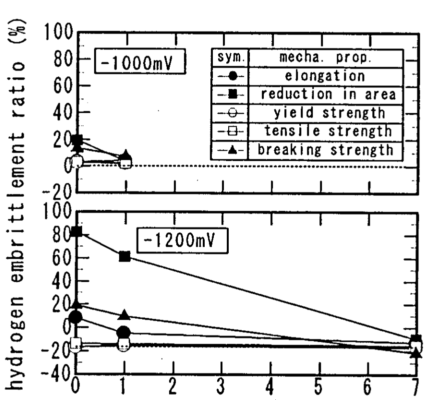


Figure 11 Recovery from Hydrogen Embrittlement (Series IV)

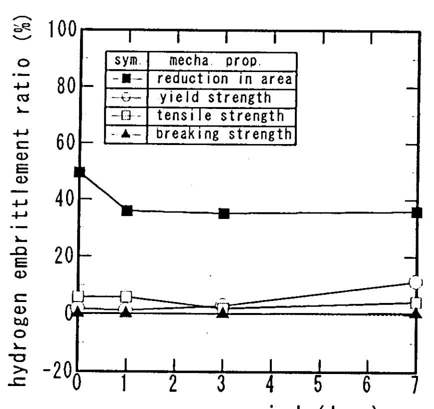


Figure 12 Recovery from Hydrogen Embrittlement (Series V)

In the series V tests, slow-strain tensile tests were implemented without cathodic polarization. Specimens had not been subjected to cathodic polarization, after keeping them in concrete for one, three, and seven days after the current flow had stopped. Figure 12 shows the test results. In the series IV tests, mechanical properties recovered after one day. In the series V tests, however, they showed slight signs of recovery but failed to recover completely even after seven days. This difference may be caused by (1) the higher volume of hydrogen occluded during the long exposure period and (2) the difference in recovery conditions between aqueous solution and concrete.

In actual structures, even if electrical erosion dose occur because of over-protection, it will be possible to recover the mechanical properties by temporarily stopping the current and thus avoiding conditions which cause hydrogen evolution. To determine the recovery period, however, it is important to take into account the potential and how long the over-protection condition persisted.

6. Volume of Occluded Hydrogen

In high-tensile steel materials such as PC steel, hydrogen embrittlement is caused by the presence of hydrogen in the material. To clarify the various factors that cause hydrogen embrittlement, it is important to assess not only the volume of hydrogen occluded in the steel, but also the hydrogen's penetration and emission behaviors. In the series V tests, therefore, the hydrogen occluded in PC wires was measured by the vacuum heating method at zero, one, three, and seven days after the current flow stopped. Figures 13 and 14 show the measured results. Table 4 shows the total volume of hydrogen emitted over three temperature ranges, which were set to appropriately assess the different peak emissions in Figure 13.

In Figure 13, the hydrogen emission curve gradually slopes upward as the temperature rises, reaching a peak at about 180℃. After a decrease in emission, the curve again increases to a peak at about 280℃. Two more peaks appear at about 400℃ and 550℃. The hydrogen in PC steel is two forms[5]. One is an unstable hydrogen that diffuses at temperatures of 250℃ or lower. This type is called "diffusive hydrogen," and plays a direct role in hydrogen embrittlement. The other is a stable hydrogen that diffuses at 250℃ or over. This type is called "nondiffusive hydrogen," and plays no role in hydrogen embrittlement[13]. A study reports that, for some steel materials, the hydrogen emitted in the second peak is also related to hydrogen

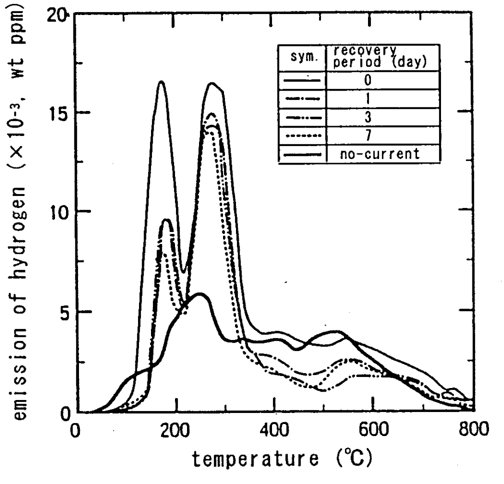


Figure 13 Hydrogen Emission Curve (Recovery Period)

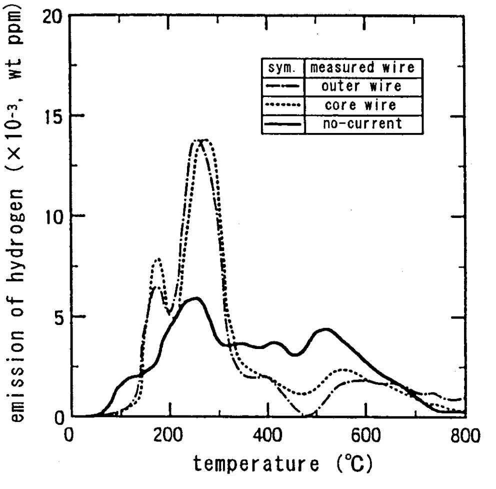


Figure 14 Hydrogen Emission Curve (Outer Wire and Core Wire)

embrittlement[10].

According to this study, the hydrogen at the first peak it is trapped weakly by dislocations, and that at the second peak trapped strongly by inclusions. When the emission curve is compared with that of the no-current specimen, it is clear that the hydrogen at the second peak is caused by cathodic polarization during the long exposure period. With the specimen left in concrete for one day, the first hydrogen peak is clearly lawer. With the specimens left in concrete for three and seven days, however, this peak did not decrease. Looking at the total volume emitted at the first peak, it has reduced for the one-day specimen, but not for the three-day and seven-day specimens, as can be seen in Table 4. The volumes of hydrogen emitted in the first peak in the case of the three-day and seven-day specimens were almost the same as for the no-current specimen. In the case of the seven-day specimen, however, the emission curve exhibits more conspicuous peaks, though the volume emitted at the first peak itself is the same as for the no-current specimen, indicating that trapped hydrogen was present even seven days after the current flow had stopped. Judging from the hydrogen emission curves and the volume of emitted hydrogen, therefore, diffusive hydrogen seems to have been present even seven days after the current flow had stopped.

Table 4 Temperature and Volume of Emitted Hydrogen

Recovery Period (Day)	R.T.-220℃	220-480℃	480-800℃	Total
0	0.26	0.42	0.17	0.85
1	0.10	0.32	0.11	0.53
3	0.12	0.31	0.09	0.52
7	0.08	0.29	0.10	0.47
No-Current	0.07	0.22	0.15	0.44

(R.T. : Room Tempareture, Unit : wt ppm)

Y. Yamakawa et al.[14] reported that, when hydrogen penetrates PC steel of the same type used in this study in an FIP test[15], the ratio of hydrogen embrittlement increased when the volume of diffusive hydrogen reached 0.2 cc/100 g.Fe. This volume of hydrogen is equivalent to 0.18 ppm, which is the volume of hydrogen emitted immediately after current flow stopped in this study.

Compared with the first emission peak, the second peak tends to be slower, presumably because it represents the emission of hydrogen (1) trapped strongly, as mentioned above, and (2) emitted after the first peak, meaning that the remaining was small. This indicates that the hydrogen emitted at 280℃ began to be emitted before the hydrogen emitted at 180℃ had completely gone. This may be one of the reasons for the different recovery periods in the series IV and V tests. (1) The first peak appeared at about 280℃, which is not high enough to clearly distinguish the emission of the nondiffusive hydrogen from that of the diffusive hydrogen. (2) When there was a one-day recovery period, a second peak was emitted, though at a low speed. (3) When there was a recovery period of seven days, the effect of hydrogen embrittlement on area reduction ratio was as large as 35%, though the volume of diffusive hydrogen was approximately the same as that for the no-current specimen. When these three observations, (1), (2), and (3), are taken into account, it appears conceivable that the second hydrogen peak also affects embrittlement.

The strand used was composed of a core wire and six outer wires. It is reported that most of the current flows in the outer wires. If so, the amount of hydrogen occluded in the core wire may be less than that in the outer wires. Figure 14 compares the hydrogen emission curves of the core and outer wires for the seven-day specimen. These two curves are almost the same, suggesting that hydrogen generated by cathodic polarization is occluded not only in the outer wires but in the core wire as well.

7. Applicability of Cathodic Protection to PC structures From the Viewpoint of Hydrogen Embrittlement

Cathodic protection technologies generally find expression in one of two methods : the galvanic anode method and the impressed current method. The impressed current method can be further divided into three : constant current, constant voltage, and constant potential methods.

In a galvanic anode system, the potential of the steel is no lower than the natural potential of zinc (about -1,000 mV) or the potential of anodic polarization of zinc due to current[16]. Therefore, it is a safe and effective means of preventing electrical erosion due to over-protection. However, it must be noted that the PC steel will be polarized to a potential lower than the hydrogen evolution potential when (1) the concrete is wet or (2) the pH of the concrete around the steel has decreased due to carbonation. It is likely, but not yet clarified, that the current flow increases the alkalinity of the concrete around the PC steel.

In an impressed voltage system using the constant current method, it is necessary to adjust the current to maintain appropriate protection, since the polarization of the steel changes depending on environmental conditions. It is also necessary to install reference electrodes and to branch the circuit appropriately at the system design stage in order to reflect the environment to which the concrete structure is exposed and to take into account the changes in the condition. There are several reasons for this stipulation: (1) measurements can be made only in the vicinity of an embedded electrode; (2) conditions differ from area to area within the concrete structure; and (3) the polarization of steel differs depending on the overall conditions in the concrete structure. Although C.C. Kumria et al.[]18 reported that the constant current method is unsuited to protecting PC structures against electrical erosion, the method would appear to be applicable if appropriately designed as outlined above. As clarified in this study, it is important to take inspection frequency into account, since the length of exposure to conditions of hydrogen evolution determines the steel's susceptibility to hydrogen embrittlement and the period needed to recover mechanical properties.

Various types of PC steel materials are manufactured using different processes, including PC steel wires and strands and PC steel bars (rolled, heat-treated, and solid-drawn). Only some of these were tested in this study. The others would seem to exhibit the same tendencies of hydrogen embrittlement when subjected to cathodic polarization to a potential lower than that at which hydrogen evolution take place. Metallurgically, however, heat-treated steel bars have a martensite texture which is more susceptible to hydrogen embrittlement than the specimens tested in this study [19]. Stress also affects the material's susceptibility to hydrogen embrittlement. These factors thus make it important to know the type of PC steel materials used in the structure to be protected.

PC structures can be classified as pretension and post-tension types. For the latter, the principle of protection is to protect the sheath. If the sheath fails, current may flow into the PC steel. As clarified by the measurements of occluded hydrogen volume in the series V tests, hydrogen is occluded not only in the outer wires but also in the core. This suggests the possibility that the PC steel inside the sheath is subject to hydrogen embrittlement. Further basic research on PC structures of the post-tension type would thus seem to be required.

8. CONCLUSION

The findings of this study can be summarized as follows.

1) Conditions of hydrogen evolution are not affected by the stress on the specimen in the elastic range. Hydrogen is generated at current densities of $0.01\mu A/cm^2$ or

over while the potential is lower than that equilibrium calculated from Nernst's equation.

2) When PC wires are subject to cathodic polarization to a potential lower than -1,000 mV, their tensile strength is not affected. However, cathodic polarization dose affect the area reduction ratio, elongation percentage, and rupture strength. Similar tendencies are also seen with PC steel in actual concrete.

3) Pseudo-cleavage planes specific to hydrogen embrittlement are seen at the periphery of rupture surfaces affected by hydrogen.

4) Susceptibility to hydrogen embrittlement is affected by pH, but not by the chloride ion concentration of the aqueous solution or by dissolved oxygen.

5) Susceptibility to hydrogen embrittlement is not affected by stress in the elastic range, but seems to be affected by the period of exposure to the conditions of hydrogen evolution.

6) The mechanical properties of PC steel subjected to hydrogen embrittlement are recovered when hydrogen evolution conditions are eliminated. The time required for recovery must be determined by taking into account the state of electrical erosion due to over-protection.

7) The curve of hydrogen emitted by the vacuum heating method shows two peaks, at 180℃ and 280℃. The hydrogen emitted at both of these peaks seemed to be a caused of hydrogen embrittlement.

8) Cathodic protection is basically applicable to PC structures from the viewpoint of hydrogen embrittlement.

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