APPLICATION OF IMPRESSED CURRENT CATHODIC PROTECTION TO STAINLESS STEEL HOT-WATER STORAGE TANKS

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1. INTRODUCTION

Hot-water storage tanks that are Class 1 pressure vessels used in hotels, hospitals, factories, and similar buildings usually supply hot fresh water at a temperature of 60-80°C. Because it is fresh water, people tend to think that corrosion never occurs in these tanks if they are made of stainless steel.

Results of many studies, however, indicate that crevice corrosion and stress corrosion crackings caused from crevice corrosion, occur in crevices and welds.[1,2,3] Although there are ways to compensate for any corrosion that occurs, such as removal by grinding, build-up welding and patch-plate welding, these repair methods can lower the corrosion resistance of the part repaired, often resulting in corrosion to recur in the same place. Further, these methods have the disadvantage that they are not suitable for repairing stainless steel hot-water tanks. On the other hand, although it is widely known that the cathodic protection method is effective in preventing crevice corrosion and stress corrosion cracking in stainless steel, it is seldom actually used.

We have investigated the optimum conditions of cathodic protection – protective potential, current density, current distribution, and electrode positions – for SUS304 (type 304, UNS S30408) stainless steel tanks in the anticipated corrosive environment, and have studied the application of an impressed current cathodic protection.

2. CORROSION ENVIRONMENT INSIDE TANKS

Well water as well as tap water is generally used in hot-water storage tanks. Therefore, as the corrosion environment it is necessary to assume a Cl⁻ concentration in the range of 1000-10 ppm and a resistivity from 300-20,000 Ωcm-25°C. In addition, inside a horizontally-installed tank used for 80°C hot water, there is the temperature distribution as shown in Figure 1.[4]
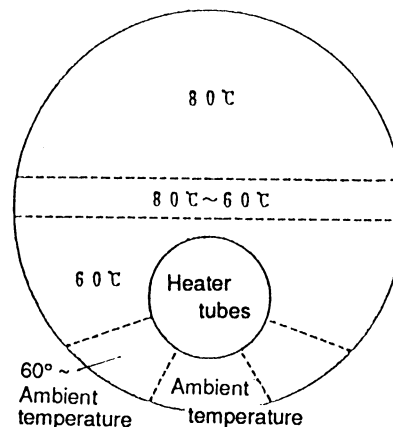

Figure 1. Temperature distribution inside a horizontally-installed tank

3. CATHODIC PROTECTION CONDITIONS

3.1 Preventive potential and current density

It has been suggested by Tsujikawa et al. that the repassivation potential E_R in crevices in stainless steel can be, at the same time, the protective potential in cathodic protection.[5,6] Therefore, we investigated the protective potential, current density, and corrosion prevention effects by E_R measurements and potentiostatic tests in the corrosive environments assumed to be in the tanks.

3.1.1 Experimental method

The material tested was commercially available type 304 stainless steel rod having a wt% composition of 18.35 Cr, 8.09 Ni, 0.55 C, 0.29 Si, 1.37 Mn, 1.37 P, and 0.030 S. The rod was processed into two nuts, one longer than the other, and a bolt; the shapes are shown in Figure 2. These were made into test pieces. Each test piece was ground with No. 240 emery paper, then degreased, and washed and kept in deionized water.

The test media were left exposed to the atmosphere and consisted of aqueous solutions of NaCl at 20, 60, and 80°C, with Cl⁻ concentration adjusted to 100, 200, 500, and 1000 ppm. Just before immersion of the test piece in

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the test solution, only the surfaces forming the gap between the long nut and the short nut were repolished with No. 240 emery paper, degreased and washed, then put into separate containers containing test solutions. While fully wet in the test solutions, the long and short nuts were tightened with a torque wrench to a torque of 1,117N·cm (120 kgf•cm). Immediately thereafter each test piece was immersed in a test solution in a test cell kept at the prescribed water temperature. The uppermost 1 cm of the long nut was left out of the solution, and E_R measurement and potentiostatic tests were carried out.

In measuring E_R, the potential was changed toward the anode at a speed of 10 mV every 2 minutes and kept for 1 hour at the potential prevailing when the current flowing in the test piece reached 200 μA. Thereafter, the potential was lowered at the same speed in the cathode direction. The changing of the potential when the current went below 5 μA was kept slow, at 10 mV per hour, and the potential was taken to be E_R when no further increase toward the anode direction was found below -5 μA.

In the potentiostatic test the test piece was transferred to a test cell and, using a potentiostat, immediately kept at the prescribed potential of -130 to -300 mV (SCE). The duration of the test was 7 days. On completion, the test piece was disassembled, and an optical microscope used to check for the presence of corrosion between the nuts. For the standard electrode we used a saturated calomel electrode at room temperature.

3.1.2 Results

Figure 3 shows the E_R values measured at a water temperature of 80°C as a function of Cl^- concentration. E_R tends to show a less-noble value as the Cl^- concentration increases, and an increase in the Cl^- concentration induces a more severe corrosion environment. To investigate the statistical dispersion of E_R, the measured values were plotted on normal probability paper. Figure 4 is an example where the Cl^- concentration is 1000 ppm. The measured E_R seems to follow a normal distribution; this was found to hold for the other Cl^- concentrations as well.
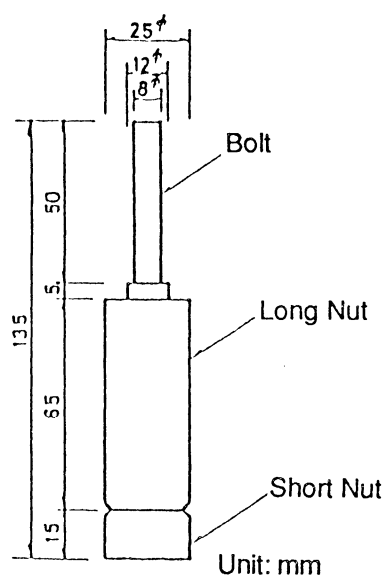

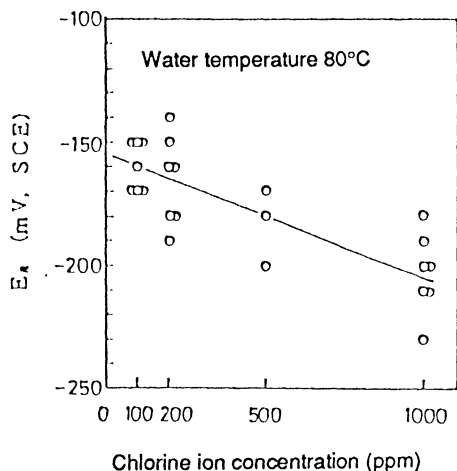Figure 2.　Shape of a test piece
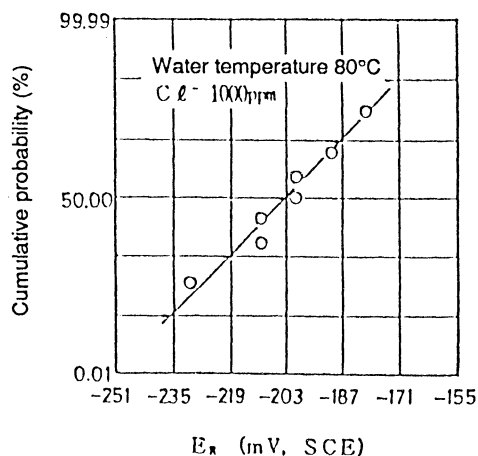

Figure 3.　Effect of chlorine ions on E_R

Figure 4.　Normal distribution plot of E_R

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Table 1 lists the least-noble value, average value, standard deviation, and -3σ value for the E_R measured at each Cl⁻ concentration.

Figure 5 shows the E_R values measured at a Cl⁻ concentration of 100 ppm, as a function of the water temperature. As the water temperature rises, the E_R tends to assume a less-noble value. This indicates that an increase in the water temperature, like an increase in the Cl⁻ concentration, makes the corrosion environment harsher.

Table 2 lists the presence or absence of corrosion on the nut crevice surface after potentiostatic tests performed at a water temperature of 80°C and at Cl⁻ concentrations of 100, 200, and 1000 ppm. Only slight corrosion was observed on the nut surfaces which had been set to the lowest value of the measured E_R or to a potential 10-20 mV less-noble than the lowest value. The propagation of the corrosion had stopped where repassivation might have occurred. But since the measured E_R have a statistical distribution, as shown in Figure 4, it was considered dangerous to take the corrosion prevention potential as the least-noble measured value of E_R. Instead, we took the -3σ value as the protective potential.

Figures 6 and 7 show how the current density changes with time in the potentiostatic tests. The current decreased after commencement of the test and then showed a generally constant value. The constant value at the above-mentioned protective potential was 8 mA/m² at a Cl⁻ concentration of 100 ppm, and 20 mA/m² at 1000 ppm Cl⁻.

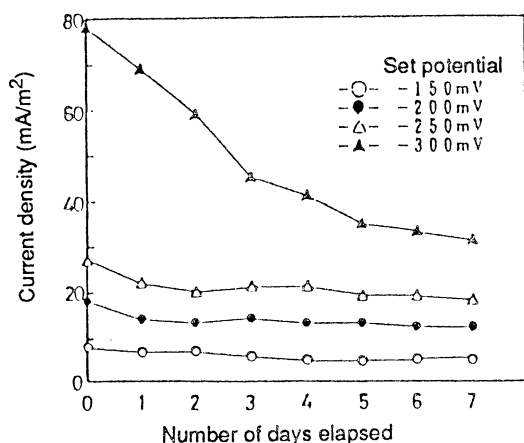Table 1 E_R values at various chlorine ion concentrations

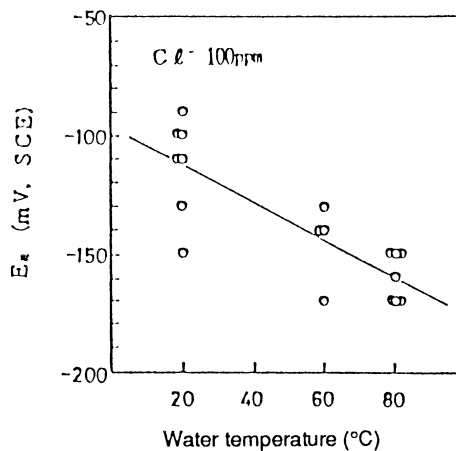| E_R (mV)	Chlorine ion concentration (ppm)			
	100	200	500	1000
Least-noble value	-170	-190	-200	-230
Average value	-160	-166	-183	-202
Standard deviation	10	18	15	16
-3σ	-190	-220	-230	-250

Figure 5. Effect of water temperature on E_R

Table 2 Corrosion occurrence in potentiostatic tests

[empty circle]: no corrosion, [filled circle]: corrosion

Chlorine ion concentration (ppm)	Set potential (-mV, SCE)						
	130	150	170	190	200	250	300
100	●○	○○	○○	○○	—	—	—
200	●	●●●	—	—	○○○	○○○	—
1000	—	●●	—	—	●●●	○○○	○○

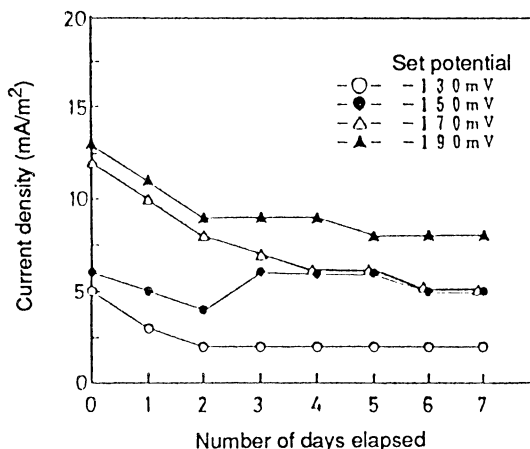Figure 6. Current density vs. time in potentiostatic tests, Cl⁻ concentration 1000 ppm

Figure 7. Current density vs. time in potentiostatic tests, Cl⁻ concentration 100 ppm

As mentioned, the corrosion environment for a hot-water storage tank must be considered over a broad range of water temperatures, Cl⁻ concentrations, and resistivities. As a protective potential for type 304 steel in all these corrosion environments, it is safe to adopt -250 mV at the most severe environmental conditions of a water temperature of 80°C, a Cl⁻ concentration of 1000 ppm, and a resistivity of 300 Ωcm-25°C. But in a high resistivity environment with a Cl⁻ concentration of 10 ppm and a resistivity of 20,000 Ωcm-25°C, the distribution of potential is more severe, so many electrodes would be needed to maintain -250 mV over the entire inner surface of the tank. Further, doing so would be uneconomical.

The test results show that the protective potential depends on the harshness of the environment. Accordingly, for safety consideration, we adopted as the protective potential for a high-resistivity environment the protective potential of -190 mV at a water temperature of 80°C, a Cl⁻ concentration of 100 ppm, and a resistivity of 3000 Ωcm-25°C. The corrosion prevention current density is discussed below.

3.2 Distribution of the potential and positioning of the electrodes

The protective potential for type 304 stainless steel was set at -190 mV in a high resistivity environment having a resistivity of 20,000 Ωcm-25°C, and at -250 mV in a low resistivity environment having a resistivity of 300 Ωcm-25°C. But to keep the entire inside surface of the tank at the protective potential, the electrodes must be positioned so as to provide an appropriate potential distribution.

Although it would be preferable to study the distribution of potential by current-passing experiments using actual tanks, an adequate study of this type is ruled out by the difficulty of controlling the environmental conditions, especially the resistivity of the solution. On the other hand, with regard to inferring the potential/current distribution by electro-conductive paper, Laplace transform solutions can be obtained relatively easily, albeit in two dimensions, even for systems having relatively complex boundary conditions. This suggests that it would be effective to apply this to cathodic protection design.[7]

So, after having confirmed there is good correspondence between the distribution of potential as determined from electro conductive paper and the actual measured value, we studied the potential distribution within tanks and set standard electrode positions. As for a preset condition, we presumed the use of a platinum-plated titanium electrode (Pt-Ti electrode) 1.5 mm in diameter, as the electrode for cathodic protection.

3.2.1 Comparison between distribution of potential as determined with electro-conductive paper and the actual measured values

The water tank tested is made of type 304 stainless steel and is 400 mm in diameter and 600 mm in height. Its base is coated with silicone rubber; the portion tested is only the side wall. The Pt-Ti electrode is installed midway between the center and the wall of tank, and the test solution is tap water having a water temperature of 80°C and a resistivity of 1900 Ω•cm-25°C.

Representation onto the electroconductive paper for 1/2 of the system in 1/4 scale is shown in Figure 8; 1 V was impressed as the voltage between the electrodes. As a boundary condition for the electrode surface, linear polarization is applied for the anode and cathode as shown in Figures 9 and 10, respectively; the parameters are given in the diagrams. For the anode at 1/4 scale, because of the small diameter of about 0.4 mm and the small anode polarization parameter La of 0.05 mm, the anode polarization was ignored and the representation was done by placing on the electroconductive paper a copper wire whose tip diameter was set to about 0.4 mm. From the
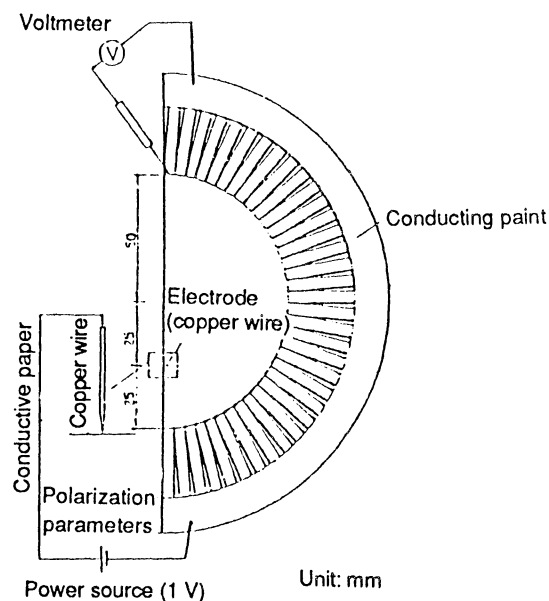

Figure 8. Representation of test conditions onto electro-conductive paper
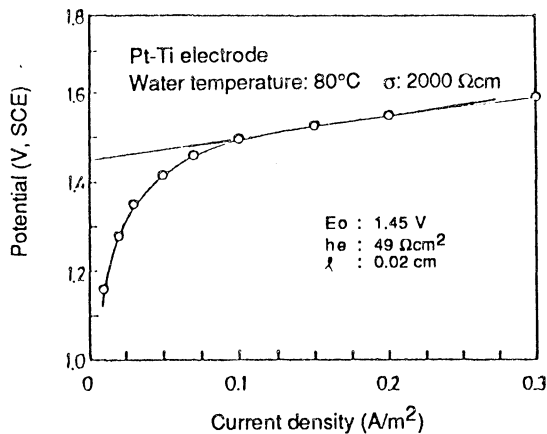
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Figure 9. Anodic polarization characteristics of Pt-Ti electrode

Figure 10. Cathodic polarization characteristics of type 304

measurement results shown in Figure 11 it was confirmed that the estimate of potential distribution obtained from electroconductive paper agrees well with the actual measured values.

3.2.2 Distribution of potential within the tank

Within a horizontal hot-water storage tank there is a temperature distribution as shown in Figure 1. In addition, inside the upper part of the tank are copper heater tubes and sockets for discharging the hot water. One half (because of the symmetry of the system) of the interior of such a tank was reduced to 1/10 scale and represented on electroconductive paper, Figure 12. Its boundary conditions are:

1) The temperature distribution within the tank was set to 20, 60, and 80°C.
2) As shown in Figures 13 and 14, linear polarization was adopted for the electrochemical properties of type 304 at water temperatures of 20, 60, and 80°C and for
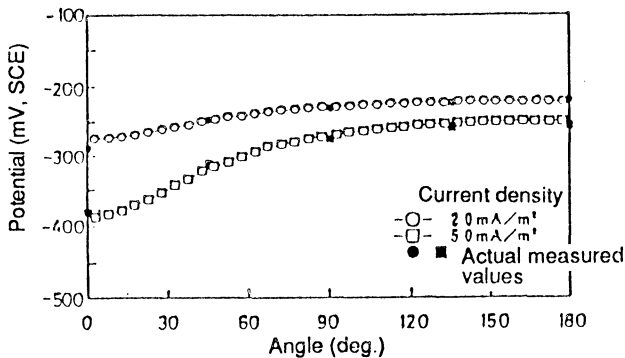
copper at a water temperature of 80°C; the parameters are listed in the diagrams.
The linear polarization and parameters shown in Figure 8 were adopted for the Pt-Ti electrode.

3) With regard to differences in resistivity due to water temperature, the high resistivity portion was made to correspond by making a hole in the electroconductive paper so as to cause the ratio of resistivity on the electroconductive paper to agree with the ratio of resistivity in the actual environment. For the polarization parameters of the high resistivity portion, the ratio with the minimum resistivity was

Figure 11. Relationship between distribution of potential as obtained from electroconductive paper and the actual measured values

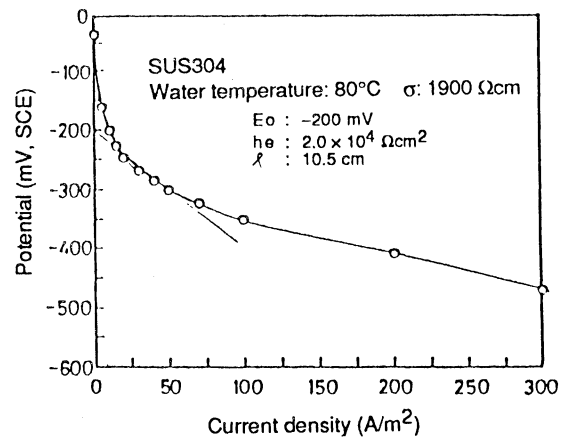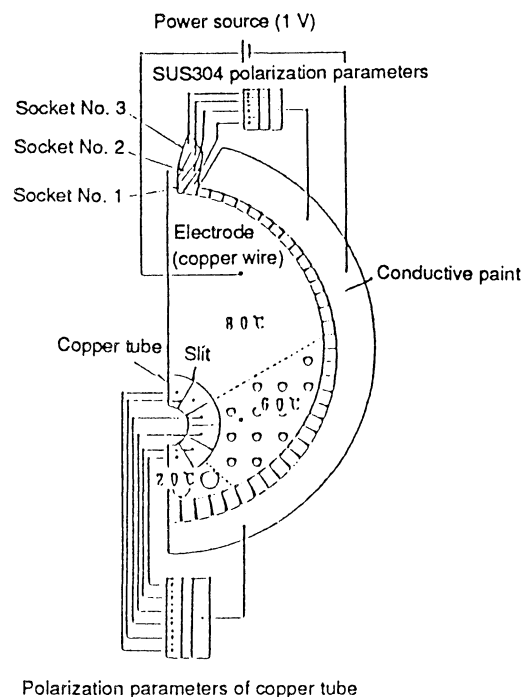Polarization parameters of copper tube

Figure 12 Representation of interior of the tank onto electroconductive paper
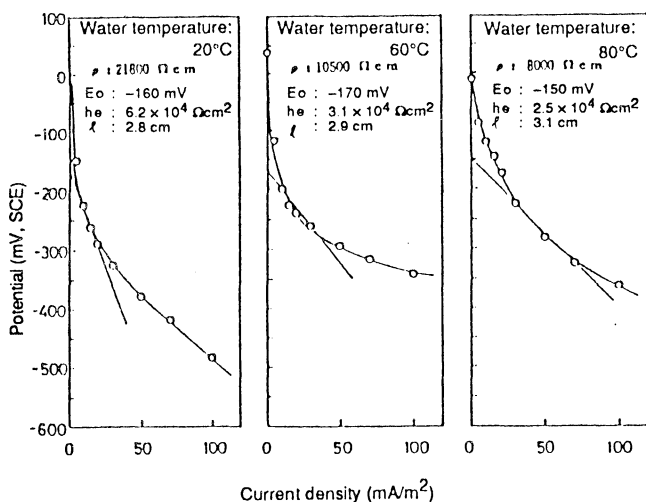
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Figure 13. Cathodic polarization characteristics of type 304 Water temperature: 20, 60, 80°C
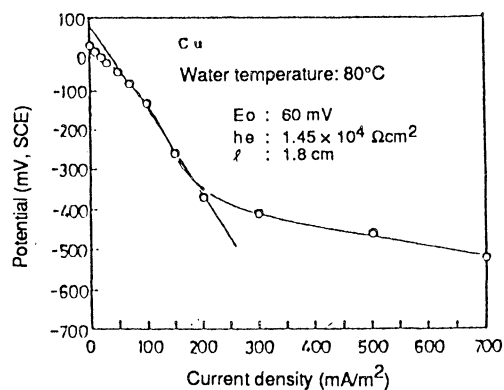

Figure 14. Cathodic polarization characteristics of copper Water temperature: 80°C

multiplied by the actual polarization parameter, and the product was taken as the polarization parameter.

4) For the polarization parameters of sockets and heater tubes that, because of their shape, cannot be indicated on the same electro-conductive paper, the representation was done by subdividing the relevant part and using a lead to connect each of the subdivided parts with polarization parameters set on a separate paper.

5) The difference in potential between the type 304 and the heater tubes was set to 0.

As an example of measurements made with electroconductive paper, Figure 16 shows a distribution of potential under the conditions given in Table 3 and Figure 15. In a low resistivity environment where the resistivity is 300 Ωcm-25°C, the distribution of potential around the circumference of the tank is uniform. But with the installation of four electrodes, the area adjacent to sockets, where the distribution of potential is poor, did not reach the protective potential. However, with the installation of six electrodes even the sockets generally reached the protective potential. In a high resistivity environment where the resistivity is 20,000 Ωcm-25°C the distribution of potential is non-uniform, but installing six electrodes improved the distribution of potential, and all parts of the inner tank reached the protective potential. Thus, the number of electrodes needed for a tank 1200 mm in diameter was taken to be six.

By examining the distribution of potential in this way, we determined the standard number and positioning of the electrodes (anodes) as shown in Table 4. The current density was set to 60 mA/m^2, based on the facts that 30-50% of the protective current flows into the heater tubes and that the distribution of current is non-uniform.

Table 3 Conditions for measurement of distribution of potential

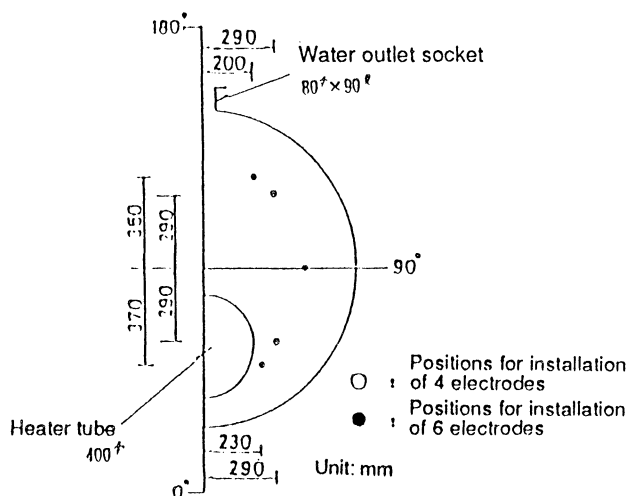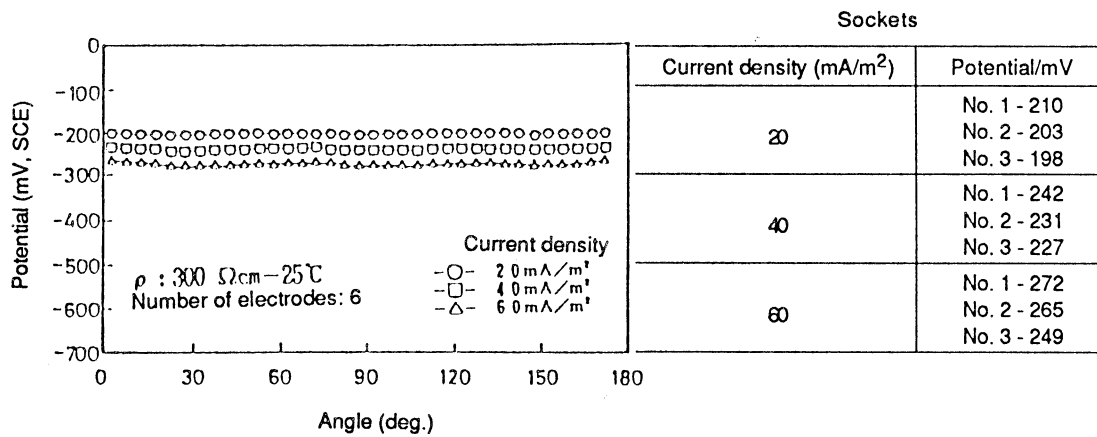| Tank diameter (mm)	1200
Diameter of heater unit (mm)	400
Resistivity of the environment (Ωcm-25°C)	300, 20000
Water temperature (°C)	80
Number of electrodes (anodes)	4, 6

Figure 15. Electrode positioning

Sockets

Current density (mA/m²)	Potential/mV
20	No. 1 - 201 No. 2 - 198 No. 3 - 194
40	No. 1 - 232 No. 2 - 225 No. 3 - 218
60	No. 1 - 263 No. 2 - 253 No. 3 - 240

ρ : 300 Ωcm−25°C
Number of electrodes: 4

Current density
−O− 2 0 mA/m²
−□− 4 0 mA/m²
−△− 6 0 mA/m²

Potential (mV, SCE) vs Angle (deg.)

Sockets

Current density (mA/m²)	Potential/mV
20	No. 1 - 210 No. 2 - 203 No. 3 - 198
40	No. 1 - 242 No. 2 - 231 No. 3 - 227
60	No. 1 - 272 No. 2 - 265 No. 3 - 249

ρ : 300 Ωcm−25°C
Number of electrodes: 6

Current density
−O− 2 0 mA/m²
−□− 4 0 mA/m²
−△− 6 0 mA/m²

Potential (mV, SCE) vs Angle (deg.)

Sockets

Current density (mA/m²)	Potential/mV
20	No. 1 - 194 No. 2 - 189 No. 3 - 179
40	No. 1 - 219 No. 2 - 207 No. 3 - 189
60	No. 1 - 243 No. 2 - 226 No. 3 - 198

ρ : 20000 Ωcm−25°C
Number of electrodes: 4

Current density
−O− 2 0 mA/m²
−□− 4 0 mA/m²
−△− 6 0 mA/m²

Potential (mV, SCE) vs Angle (deg.)

Sockets

Current density (mA/m²)	Potential/mV
20	No. 1 - 200 No. 2 - 197 No. 3 - 181
40	No. 1 - 229 No. 2 - 224 No. 3 - 193
60	No. 1 - 159 No. 2 - 251 No. 3 - 204

ρ : 20000 Ωcm−25°C
Number of electrodes: 6

Current density
−O− 2 0 mA/m²
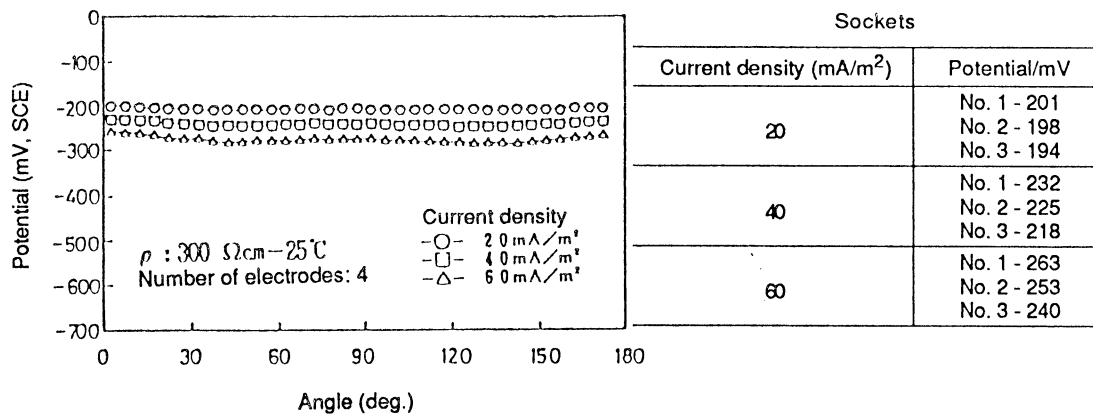−□− 4 0 mA/m²
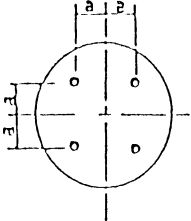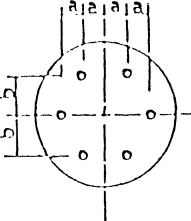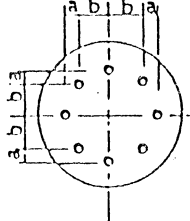−△− 6 0 mA/m²

Potential (mV, SCE) vs Angle (deg.)

Figure 16. Results of measurement of potential distribution using conductive paper

Table 4 Standardized number and positioning of electrodes

Tank diameter	800 - 1099 mm	1100 - 1599 mm	1600 - 1999 mm
Number of electrodes	4	6	6
Positioning of electrodes	a: 150 - 250 mm	a: 180 - 300 mm b: 300 - 530 mm	a: 170 - 220 mm b: 380 - 530 mm

4. OUTLINE OF CONSTRUCTION WORK FOR IMPRESSED CURRENT CATHODIC PROTECTION SYSTEM.

Figure 17 shows a impressed current cathodic protection system. The important points and characteristics are as follows:

1) The electrodes used are long, wire-shaped Pt-Ti electrodes having a diameter of 1.5 mm with a plating thickness of no less than 1.0 μm platinum.

2) Installation of the electrodes is done by stringing them, using electrode supports attached by welding, to the surface of the tank inner wall. This technique allows the electrodes to be positioned appropriately for corrosion prevention and made the protective current distribution more uniform.

3) T-shaped elbows and electrode plugs are used for extending the electrode terminals to the exterior of the tank. This method made it possible to do the construction work on an already installed tank.

4) Diodes are attached to a connection box that is in electrical continuity with the tank, preventing reverse connection with the Pt-Ti electrodes.

5) On the concave parts of heater tubes and manifolds, where the installation of Pt-Ti electrodes may be difficult, rust prevention is done using a magnesium anode.

6) A single-phase, a full-wave-rectification power source is used, having input of AC 100 V or 200 V and output of DC 3-12 V and 5A or 10 A.
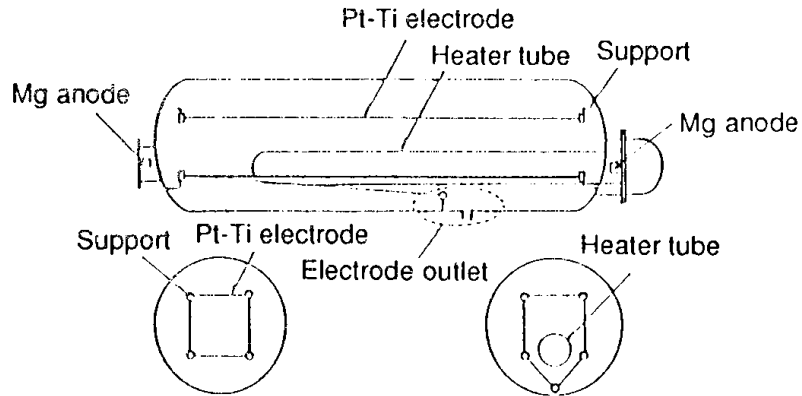
5. CATHODIC PROTECTION EFFECTS AND CONSTRUCTION RESULTS

Among the stainless steel hot-water storage tanks to which we applied impressed current cathodic protection systems were type 304 tanks that had leaked due to pre-existing cracking near the welds. For such tanks the leaks were first repaired, for example, by patch-plate welding, then the cathodic protection system was applied. Since that time no occurrence of corrosion was found even in the annual performance inspection required for Class 1 pressure vessels. They are still in use after 5 years' time. Such remarkable effectiveness in corrosion prevention has been recognized, and cathodic protection has now been applied to about 5000 stainless steel hot-water storage tanks.
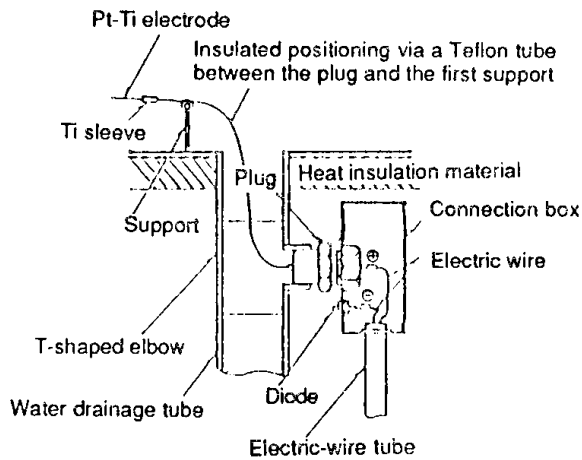
6. CONCLUSION

We have presented the cathodic corrosion prevention conditions for stainless steel hot-water storage tanks and an outline of the cathodic protection method.
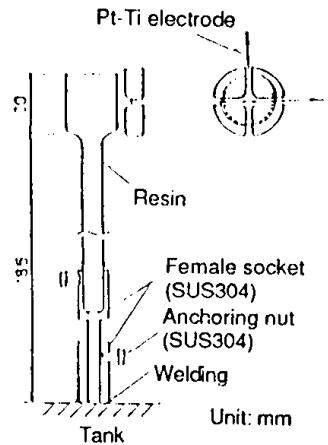
Even type 304 stainless steel, which is in general use today, can, through suitable cathodic protection, be a material with superior durability. However, proper cathodic protection requires that attention be given to electrode positioning and tank structure so as to have uniform distribution of potential.

Pt-Ti electrode

Heater tube Support

Mg anode

Mg anode

Support Pt-Ti electrode

Electrode outlet

Heater tube

Detailed diagram of electrode outlet

Pt-Ti electrode

Insulated positioning via a Teflon tube between the plug and the first support

Ti sleeve

Plug Heat insulation material

Support

Connection box

Electric wire

T-shaped elbow

Water drainage tube Diode

Electric-wire tube

Shape of electrode support

Pt-Ti electrode

Resin

Female socket (SUS304)

Anchoring nut (SUS304)

Welding

Tank Unit: mm

Figure 17. Example of construction of the impressed current cathodic protection system

References

1) M. Taneda, Equipment and Management, 15, 3, 37 (1981)
2) T. Kanyo, G. Takabe, Nisshin Steel Technical Report, 42, 60 (1980)
3) K. Harada, "Boshoku Gijutsu", 18, 297 (1969)
4) M. Hachiya, "Netsukanri", 19, 9, 37 (1967)
5) S. Tsujikawa, K. Hisamatsu, "Boshoku Gijutsu", 29, 37 (1980)
6) S. Tsujikawa, Tsuneo Hari, K. Hisamatsu, "Boshoku Gijutsu", 32, 149 (1983)
7) K. Mochizuki, T. Shirouzu, S. Hiratsuka, "Boshoku Gijutsu", 33, 573 (1984)