INVESTIGATION OF MONITORING TECHNOLOGIES FOR HEAT TRANSFER CORROSION IN REPROCESSING EQUIPMENT

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Abstract： Two types of in-situ monitoring techniques using electrical resistance methods were developed for estimating the wall thinning of heat transfer tubes used in evaporators for Purex process on commercial reprocessing plants. The corrosion rate is accelerated with oxidizer ions formed by the thermal decomposition of nitric acid under heat flux. An in-situ corrosion sensor was developed for estimating the corrosion rate of heat transfer tubes using miniature heat transfer tube specimens under heat flux control. It is possible to simulate the heating condition as same as heat transfer tubes. The applicability was evaluated by setting it in gas –liquid separator in a mock-up evaporator for acid recovery. The sensitivity of electric resistance methods is increased with decreasing the residual thickness of probe tube. The other is the electrical potential drop method using direct current so-called the field signature method. It is applicable to estimate the corrosiveness of reprocessing nitric acid by setting it on the drain tube in evaporator. The sensitivity to the thinning rate of tubes wall machined artificially was obtained within ±10% to the wall thickness. It has the non-sensitive region nearly 0.1mm up to begin working. The practical applicability has been also evaluated by setting it in a mock-up evaporator.

Introduction： On the commercial reprocessing plant using Purex process, sufficient corrosion resistance is required to equipment materials used in nitric acid solutions including oxidizer ions derived from spent nuclear fuels[1~3]. Reprocessing grade Type 304ULC austenitic stainless steel has been used in BNFL type evaporator for nitric acid recovery and for concentrating the radioactive solutions. These are operated at low boiling point by reducing the system pressure for reducing the corrosiveness. However, heavy inter-granular corrosion was experienced in the inner wall of heat transfer tubes in the mock-up evaporator for nitric acid recovery during operated 26,700 hrs [4]. The corrosion mechanism was interpreted as the corrosion acceleration effect duo to the formation of oxidizer ions on heat transfer surfaces. The formation of high oxidizing atmosphere is dependent on the metal surface temperature and the heat flux in relation to the thermal decomposition of nitric acid under boiling.

The development of corrosion monitoring technologies for these heat transfer tubes is required to establish the maintenance technology of the equipment. A lot of works[5~7] have been reported on the corrosion monitoring techniques based on electrical potential drop method or electric resistance method. However, the investigation concerning about the practical applicability for in-situ corrosion monitoring under heat transfer condition has not almost been carried out. The present study has undertaken to evaluate the practical applicability of two types of in-situ corrosion monitoring system selected by the preliminary examination for screening. One is field signature method (so-called FSM hereafter), which is based on sensing the electric field pattern by measuring small potential differences caused by general metal loss, cracking or pitting due to corrosion or erosion between electrode pairs set up on the surface of monitored objects [8]. The other is a corrosion sensor that is possible to simulate the heat transfer surface of tubes under heat flux control and has an electric resistance measurement system [9] (so-called the modified electric resistance method hereafter).

Experimental Procedure： It is difficult to do direct corrosion monitoring of the heat transfer tubes in the evaporator, because of welding seal and narrow gap. As the alternative monitoring method, it is possible to evaluate the corrosiveness of nitric acid solution it self, by measuring the corrosion rate of by-pass tube near heat transfer tube assembly as shown in Fig.1. In-situ corrosion monitoring method of by-pass tube by setting FSM was selected. The measured corrosion rate is possible to estimate real corrosion rate at heat transfer tubes, because the

corrosion rate is proportional to the contents of oxidizer ions formed in heat transfer tube assembly.

The schematic illustration of detection principle of FSM is shown in Fig.2. Field coefficient (FC) value is calculated by the following equation.

$$FCAi\ (ppt) = (Bs/As \times Ai/Bi - 1) \times 1{,}000$$

FCAi : FC value for electrode pair A at time i

As : voltage for electrode pair A at start-up

Bs : voltage for electrode pair B (reference) at start-up

Ai : voltage for electrode pair A at time i

Bi : voltage for electrode pair B (reference) at time i

In order to clarify the detection limit of FSM for uniform corrosion by artificial thinning, the measurement of FC value was carried out using specimens with uniform thickness loss in inner wall up to 0.05, 0.1, 0.3 and 0.5mm respectively.. The potential measuring electrodes of 2mm diameter were stud-welded on the outside of tube specimen at longitudinal axes of 0, 90, 180 and 270deg by spacing of 6, 8, 10 and 12mm respectively as shown in Fig.2.

Furthermore, the measurement of FC value was performed under the heat-transfer corrosion condition at a boiling point of 68℃ in 9 mol/dm^3 nitric acid solution containing 1,000mg/L vanadium ion. Figure 2 shows also the schematic diagram of test apparatus under heat conducting corrosion condition. The inner pressure of test-cell was controlled at 0.016MPa by a vacuum controller. The outside temperature of tube specimens was controlled at about 130℃ by electric heater. Two types of stainless tubes were tested. Table 1 shows the chemical composition of tube specimens used. One is the reprocessing type 304ULC stainless steel. The other is the commercial grade 304TP stainless steel conducted by a heat-treatment of 650℃ for 10h in order to enhance inter-granular corrosion. These tube specimens are 33mm in outer diameter 4mm in thickness. The potential measuring electrodes of 2mm diameter were stud-welded on the outside of tube specimens at longitudinal axes of 0, 90, 180 and 270 deg by spacing of 6mm. The nitric acid solution was renewed every approximately 500 h and the thickness of tube specimens was measured by ultrasonic thickness measuring system.

The suitability of corrosion sensor based on the modified electric resistance method as a purpose of practical applicability at the gas-liquid separator of nitric acid recovery evaporator was examined. An environment of gas-liquid separator is not heat conducting condition. Thus, the modified electric resistance method was consisted of heat conducting control mechanism in probe tube itself. Figure 3 shows the schematic illustration showing the modified electric resistance system for the evaluation of practical applicability in laboratory. The size of prove tube as corrosion sensor, which is the reprocessing type 304ULC stainless steel, is 29mm in outer diameter, 27mm in inner diameter and 170mm in length.

The relationship between prove tube thickness (t) and electric resistance value (= measured voltage V／applied current I) is given by the following equation. Applied alternate current is about 0.8A and 200Hz.

$$t\ (mm) = \rho \times I \times \ln (S1+L1)/S1] / V\pi$$

where, ρ is the intrinsic electrical resistivity of material.

Results and Discussion：

(1) Evaluation of practical applicability of field signature method

The simulation of FSM signal from even corrosion was performed by using commercial software tool NISA for FEM, in order to investigate the suitability of FSM for specified monitoring problem. The simulations showed that with a sensitivity of 1FC, FSM could detect an even corrosion of less than 0.03mm in tube inner. In case of even corrosion, with changing electrode spacing from 4mm to 6 and 8mm, there was not any significant change in the detected data.

The suitability of FSM for even corrosion verification by artificial thinning was evaluated experimentally. Figure 4 shows the relationship between tube inner thinning by UT measurement and FC value after machining. The tube inner thinning calculated by FC value were coincident with that measured by UT. FC value was 20% higher than that by UT measurement. This means that tube inner thinning can be detected by a sensitivity of 20%. With increasing electrode spacing, FC values became to be more scattered. The scattering band was approximately 40%. Especially, the tendency was evident in the case of a slight thinning such as 0.05mm. This means that the sensitivity of FSM is deteriorated with the increase in electrode spacing and the most suitable electrode spacing for tube wall thickness must be selected.

The evaluation of practical applicability of FSM was performed under the heat transfer corrosion condition in 9 mol/dm^3 nitric acid solution. Figure 5 shows the changes in tube inner thinning by UT measurement as a function of heat transfer corrosion time. The tube inner thinning, which is the value averaged at the same vertical axis inter- electrodes region of tube specimens, increased gradually with increasing corrosion time. The tube inner thinning at a corrosion time of 220days was approximately 0.4mm in the reprocessing type 304ULC stainless steel, while was approximately 0.7mm in the commercial grade 304TP stainless steel. The difference between tube inner thinning measured by UT and the value estimated by dissolved Ni ion concentration in the commercial grade 304TP stainless steel was larger than the difference in the reprocessing type 304ULC stainless steel. This indicates that inter-granular attack is more accelerated in the commercial grade 304TP stainless steel. Figure 6 shows the changes in FC values as a function of heat transfer corrosion time. In comparison with Fig.5, it is appear that the changes in FC values were coincident with the changes in tube inner thinning by UT measurement, thought FC values were not detected within a thinning of 0.1mm. This means that the detective minimum for even corrosion in FSM is estimated to be 0.1mm. Consequently, it is concluded that FSM is useful for in-situ monitoring technique under hear transfer surface corrosion condition. Therefore, the sensor for investigation of suitability as corrosion monitoring in demonstration testing equipments was made. And, those are installed to the by-pass tube in demonstration testing equipment of acid recovery evaporator and are evaluating now. The by-pass tube inner thinning amount estimated from FC values was coincident with the reduction of tube wall thickness measured by UT at in-service inspection as shown in Fig.7.

(2) Evaluation of practical applicability of corrosion sensor with heat conducting control mechanism

Figure 8 shows the change in electric resistance as a function of average thickness of probe tube of the modified electric resistance method. The heat conducting corrosion condition was simulated at the surface of prove tube. The electric resistance value increased with the decrease in residual average thickness of probe tube by heat transfer corrosion testing, according to theoretical equation. The difference in electric resistance value for even corrosive testing interval became to be lager, as the residual average thickness of probe tube decreased more. This means that the modified electric resistance method is more sensitive at the end of life of probe tube. The effect of environment such as temperature was examined. The electric resistance value is found to be stable for the change in probe tube inside temperature, as shown in Fig.9. The electric resistance value was also stable for continuously holding. Furthermore, there was a significant different in the electric resistance value for even corrosive testing interval, as shown in Fig.10. Thus, the modified electric resistance method was found to be useful for the monitoring technique for the evaporator of nitric acid recovery.

Conclusions：On this research, the in-situ monitoring method for detecting the wall thinning of heat transfer tubes in evaporators has investigated in order to ensure the reliability of equipment materials used in spent fuel commercial reprocessing plant. The practical applicability of field signature method (FSM) and a corrosion sensor under simulating corrosion behavior at the heat transfer surfaces so-called the modified electric resistance method (MESM) was evaluated.

(1) On FSM, the wall thinning higher than 0.1mm under heat flux control is possible to detect with the sensitivity of 20% in setting outer side of tubes. It has enough sensitivity as the indirectly

in-situ monitoring technique applied for estimating the wall thinning of heat transfer tubes in an evaporator for nitric acid recovery.
(2) On MESM, the heat transfer condition was simulated with controlling the heat flux of small length probe tubes. The electric resistance value increased according to theoretical equation with decreasing the residual average thickness of probe tube. The sensitivity was enhanced with decreasing the residual average thickness of probe tube.
(3) Above in-situ monitoring techniques has been tested in mock-up evaporator for nitric acid recovery. The sensitivity on both corrosion monitoring techniques has been obtained as same as it by laboratory experiments.

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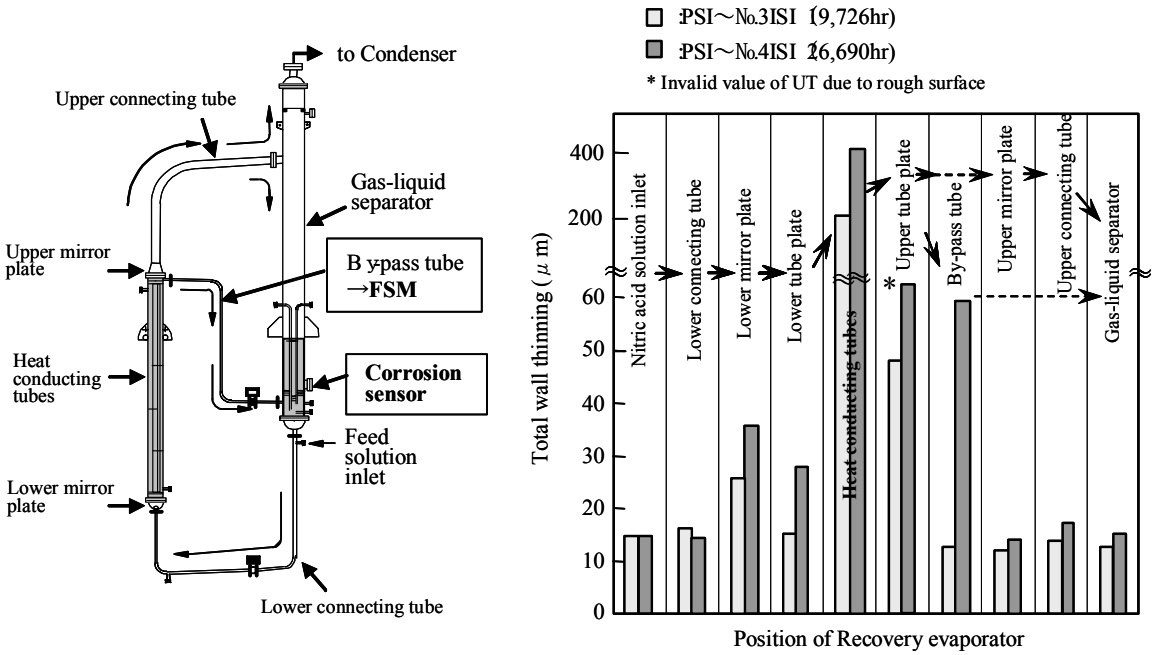


Fig.1 Schematic view of demonstration testing equipment and corrosion behavior at position in recovery evaporator

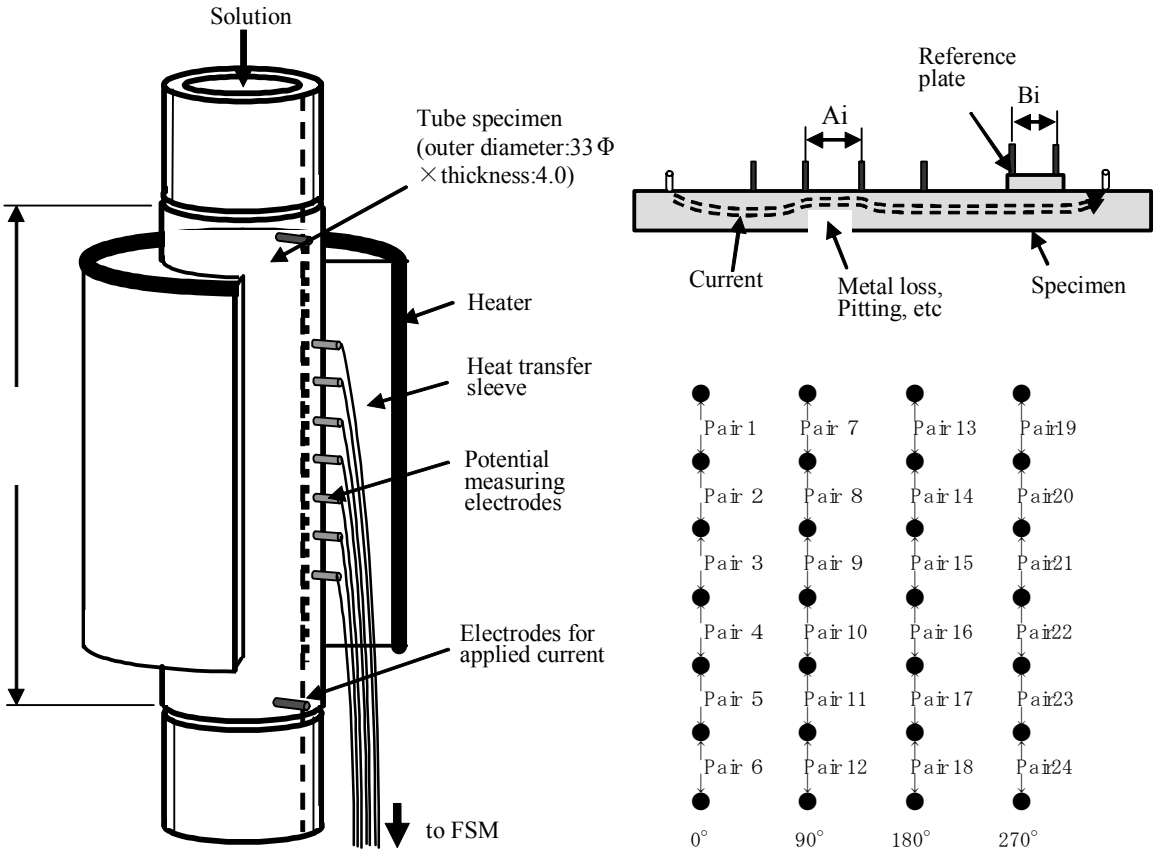


Fig.2 Schematic illustration showing testing apparatus and detection principle of field signature method

Table 1 Chemical composition of steels of tube specimens used

	C	Si	Mn	P	S	Ni	Cr
R-SUS310ULC	0.0012	0.37	1.56	0.013	0.001	10.7	18.85
SUS304TP	0.02	0.46	1.09	0.024	0.02	9.1	18.0

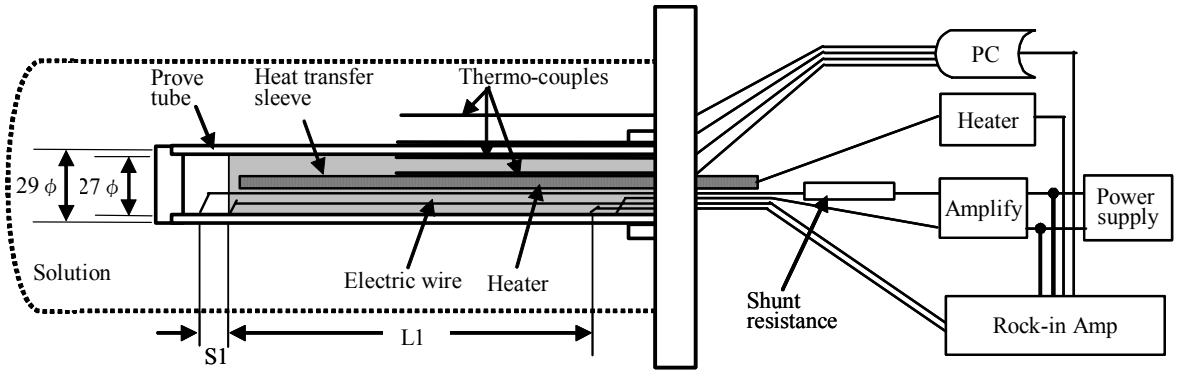


Fig.3 Schematic illustration showing prove of corrosion sensor with heat conducting control mechanism

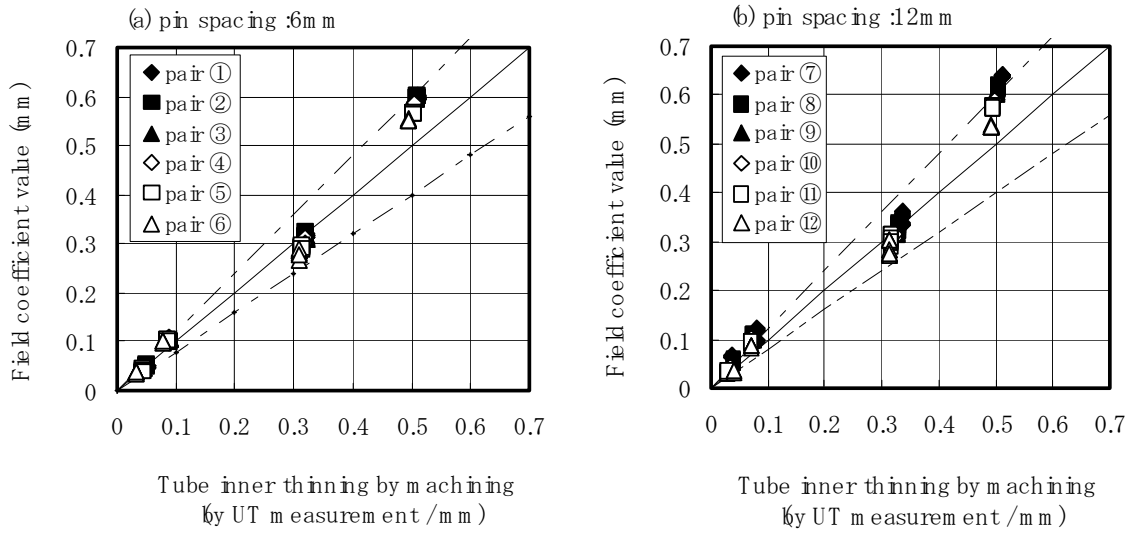


Fig.4 Relationship between field coefficient value and tube inner thinning measured by UT after machining

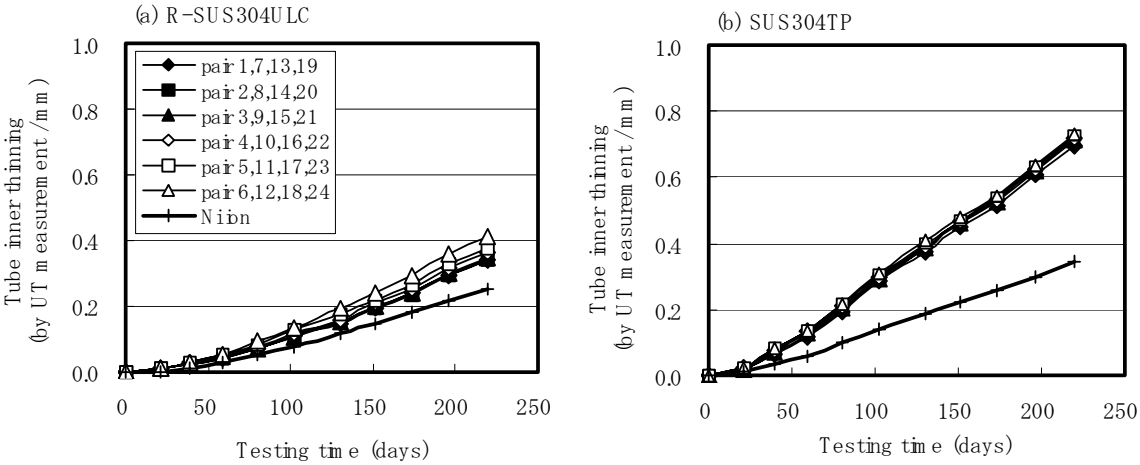


Fig.5 Change in tube inner thinning measured by UT as a function of heat transfer corrosion testing time

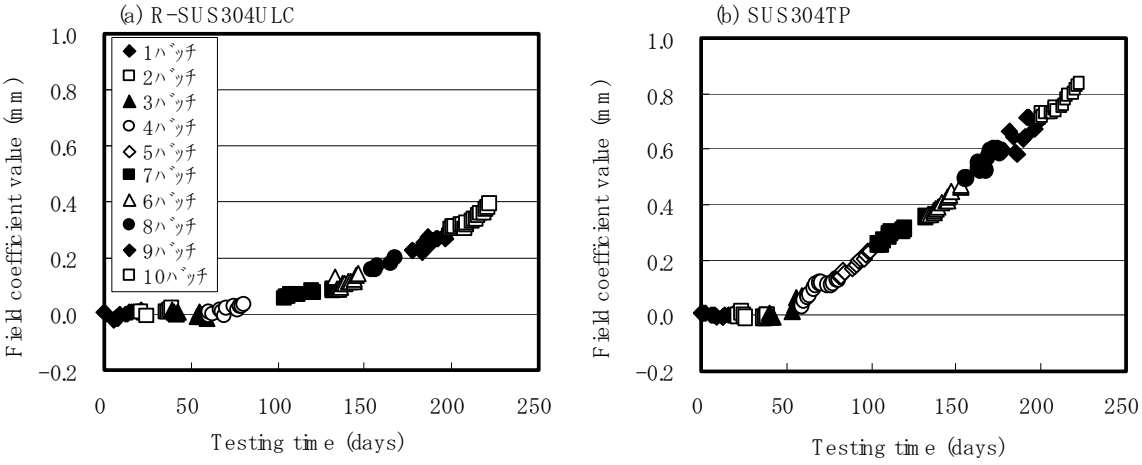
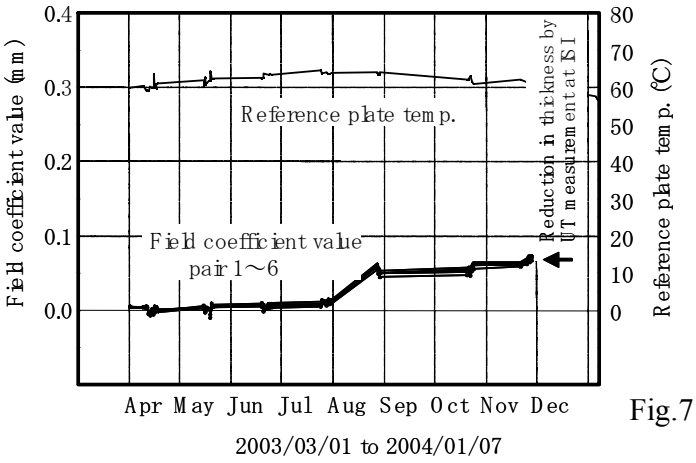


Fig.6 Change in field signature value as a function of heat transfer corrosion testing time



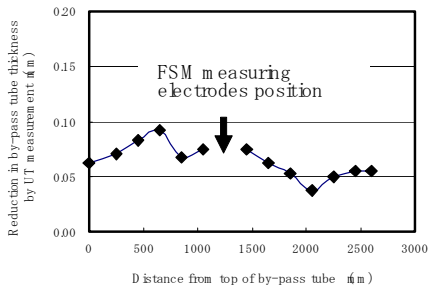


Fig.7 Change in field signature value as a function of operating time in demonstration testing equipment

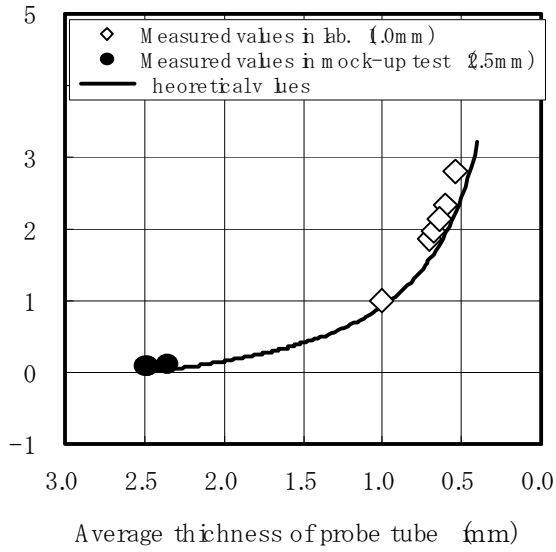


Fig.8 Relationship between electric resistance value and average thickness of prove tube

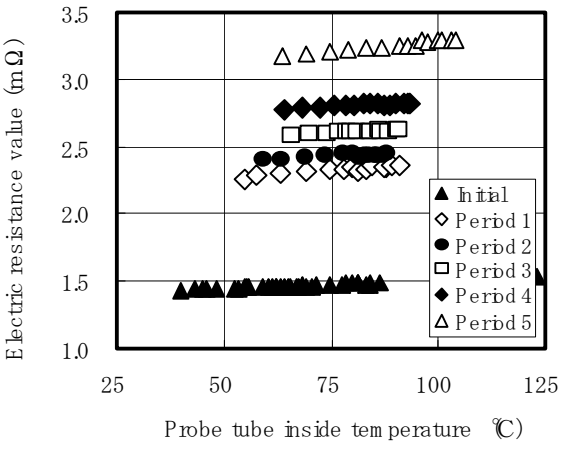


Fig.9 Relationship between electric resistance value and prove tube inside temperature

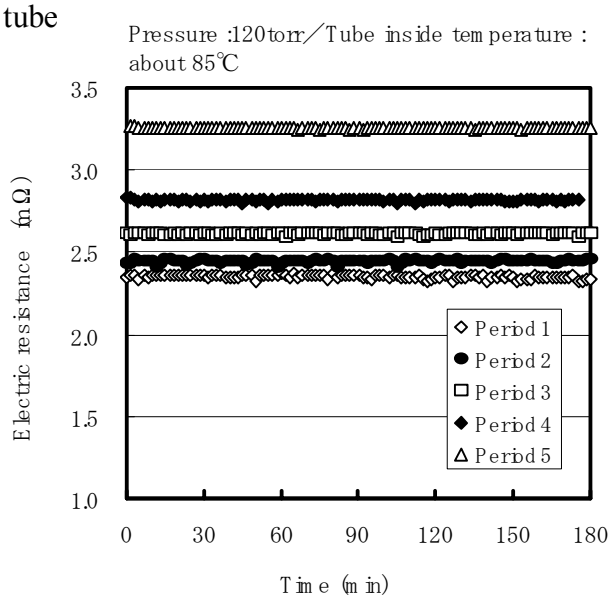


Fig.10 Change in electric resistance value as a function of testing time