

ties as expected at the design stage and achieved excellent performance with zero corrosion. In particular, at the portion equivalent to the downstream of the control valve, erosion due to turbulence was anticipated, but did not occur, confirming the excellent resistance of rubber lining to erosion. Epoxy tubes used in similar places for comparison exhibited poor resistance to erosion.

3.3 Proposal for Future Studies

3.3.1 Proposal on Metallic Materials

For actual problems, if the corrosion properties of current practical materials (copper alloys and titanium as heat transfer tubes) against seawater and brine at the site are monitored over a long period and problems occur due to corrosion, the chemistry of the seawater and brine, the history of plant operation, corrosion products and the corroded portion of metallic materials must be thoroughly investigated and causes must be elucidated. Data must be built into a data base for free retrieval. Needless to say, matters related to corrosion should be subdivided into a rather wide range, such as plant name, date of accident occurrence, operation history of the plant, chemistry of the environment, component name of equipment, metallic material name, welding process, type and characteristics of corrosion, general information on corrosion products, schematic of corroded area, etc. to enable easy retrieval. This will be greatly advantageous when the amount of data increases in the future.

For future problems, with the realization of an all aluminum MSF plant in mind, precise investigation on aluminum alloy heat transfer tubes must be carried out. The biggest problem for corrosion resistance of aluminum alloys is pitting characteristics, and the poor reproducibility of pitting phenomena in conventional experiments has impaired the reliability of aluminum alloys as a heat transfer tube material.

Freedom from pitting in aluminum alloy heat transfer tubes is the most important priority, and in that sense, plants might be operated with the brine pH held slightly to the alkali side and scales prevented by additions of strong chemicals and sponge balls.

As shown in this research report, the pitting of aluminum alloy heat transfer tubes in the aluminum plant of the Aluminum Association at Freeport tends to stop after about 3 years, but what are the causes? Pitting is less serious at the 2nd pass than at the 1st pass, and at the 3rd pass than at the 2nd pass. Is this attributable to the effects of collecting heavy metal ions? It is important to investigate the original texts of this report to find these answers, and if possible, it would be advantageous to talk with those in charge of the research at this aluminum plant.

3.3.2 Proposal on Nonmetallic Materials

There are very few examples of using cement and non-metallic materials such as FRP for MSF seawater desalination plants. Genally speaking, non-metallic materials are corrosion resist-

ant for sea-water as well as reasonable on processing and installing cost.

However, there are some cases to damage the fidelity of non-metallic materials after using them for desalination plants without checking their characteristics sufficiently. Behind the cases, we can point out the fact that there is insufficient basic data accumulation concerning corrosiveness and processing methods of non-metallic materials.

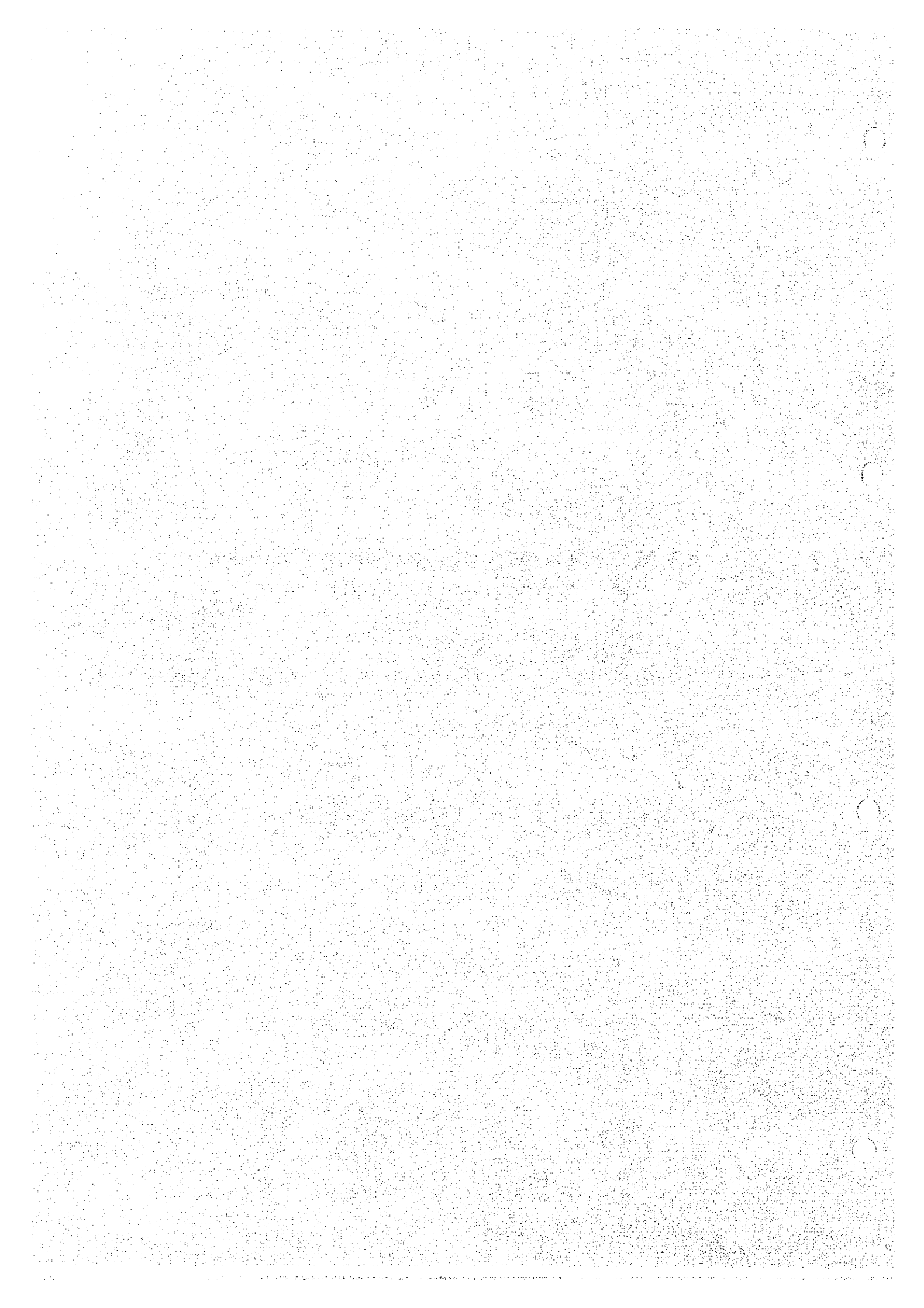
As many non-metallic materials are corrosion resistant for sea-water and resistant for pH concentration, oxygen, carbon-dioxide, hydrogen-sulfide in the sea-water which damage metallic materials, it is necessary to accumulate data of their corrosiveness and to provide experimental equipments in order to examine them.

References

1. A.H. Tuthill: Mater. Performance, 26, N. 9 (1987), 12
2. A. Cohen and P.E. George: *ibid.*, 13, No. 8 (1974), 26
3. C.F. Schrieber and F.H. Coley: *ibid.*, 15, No. 7 (1976), 26
4. D. Hirschfeld: Tech. Mitt. Krupp Werksber., 37, H. 2 (1979), 55
5. W.W. Kirk and A.H. Tuthill: NiDI Workshops, Applic. Tech no. of Cupronickel, Tokyo, (1991, Nov.), No. 4
6. Brian Todd: *ibid.*, No. 3
7. A.C. Friedland and D. Kon: Corrosion/81, paper No. 142(1981)
8. C.F. Shrieber, T.D. Boyce, B.D. Oakes and F.H. Coley: Mater. Performance. 14, No. 2 (1975), 9
9. S. Sato and K. Nagata: Sumitomo Light Metal Tech. Rep., 18, No. 1/2 (1977), 11
10. S. Sato and K. Nagata: *ibid.* 22, No. 3/4 (1981), 76
11. A.H. Tuthill: Mater. Performance, 26, No. 9 (1987), 12
12. A. Geroge and B.C. Syrett et al.: Corrosion/83, paper No. 76 (1983)
13. R. Francis: BNF Metals Technology Centre (1987), 94
14. G. Gusman and C. Simoncelli et al.: Desalination, 74, No. 1/3 (1989), 259
15. J. E. Castle and D.C. Epler: Corrosion Science, 16(1976), 145
16. H. Yamamoto, H. Kunieda et al.: Corrosion Protection Technique, 28 (1979), 485
17. K. Minamoto and S. Kyouhara: Thermal/Nuclear Power Generation, 35 (1984), 63
18. A.M.S.E. Din, D.M. Khamis and M.S. Said: Proc. 9th Int. Congr. Met. Corrosion, Vol. 3 (1984), 621

19. E.D. Thomas, M.H. Peterson and D.K. Christian: Corrosion /88, paper No. 402 (1988)
20. H. Miyamoto: Proc. 13th Mat. Struct. Forum of Japan Seawater Academy, Current Status and Problems of Heat Exchangers using Seawater (1989.11)
21. S. Yamauchi, K. Nagata and S. Sato: Proc. 7th Int. Congr. Met. Corrosion, Vol. 4 (1978), 1657
22. Y. Fukuda and M. Akashi: Proceedings of Fushoku-Boshoku/ 91, 141 (1991)
23. T. Fukutsuka, K. Shimogori, H. Satoh, and F.Kamikubo: R &D/Kobe Steel Engineering Reports, 32, No. 1 (1982), 28 (1985), 1165
24. H. Satoh: Surface Technology, 40 (1989), 1091
25. H. Satoh: Org. Japan Seawater Academy, 44 (1990), 200
26. S. Yamauchi, K. Nagata, and S. Sato: Sumitomo Light Metal Tech. Rep., 24, No. 1/2 (1983), 6
27. H. Satoh, F. Kamikubo et al.: Titanium Sci. Technol., 2 (1985), 1165
28. S. Yamamoto, Y. Soejima et al.: Hitachi Shipbuilding Engineering Reports, 44 (1983), 77
29. C. Taki and H. Sakuyama: Trans. Japan Institute of Metals, 27 (1988), 290
30. S. Kitayama and Y. Shida: Sumitomo Metal Tech. Rep., 41 (1989), 447
31. Z. Ahmed: Anti-Corros. Method Mater., 33 (1986), 4
32. Y. Watanabe, K. Nagata, S. Nakamura, and Y. Onimura: Corrosion Engineering, 25 (1976), 323
33. R.A. Bonewitz and E.D. Verink, Jr.: Mater. Performance, 14, No. 8 (1975), 16
34. G. Faninger, D. Merz and H. Winter: Int. Conf. Rapidly Quenched Metal, Vol. 2nd, No. 1 (1976), 483
35. J.R. Maurer: Proc. Sympo. Advanced Stainless Steels for Seawater Applications (1980), 11
36. R. Nemoto: Proc. 11th Mat. Struct. Forum of Japan Seawater Academy, Super Stainless Steel (1988.11)
37. J. Haruki, H. Koh et al.: Proc. 36th Corrosion Protection Symposium, (1989), 283
38. R.M. Davison and J.D. Redmond: Mater. Performance, 27, No. 12 (1988), 39
39. J. Olsson and B. Wallen: Desalination, 44 (1983), 241
40. S. Nordin, *ibid.*, 44 (1983), 255
41. M. Katahira and Y. Kaneko: NKK Engineering Reports, No. 132 (1990), 96
42. T. Hodgkiess and P.S. Chia: Proc. Twelfth Int. Sympo. Desalination and Water Reuse, Malta (1991, April), 267
43. S.V.Carleton, J.A. Manning, Jr.: Corrosion Vol. 1975 No.41, page 41/1-41-12
44. Tom G. Temperley: Desalination, 33(1980) p99-107
45. Japan Society of Corrosion Engineers: Corrosion Protection Technologies, 1976 May.

4.2 M-3 Study on Some Materials by Corrosion Measurement Apparatus



**MSF DESALINATION
LITERATURE SURVEY NO. 1, M-3**

**STUDY ON SOME MATERIALS BY CORROSION
MEASUREMENT APPARATUS**

JULY 1992

By

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SALINE WATER CONVERSION CORPORATION

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1. Introduction

In general, the metals used in plants, facilities and structures tend to be prone to deterioration, due to environmental interaction in almost all environment, and this results in the so-called phenomenon of corrosion. Fatal accidents caused due to corrosion can be avoided by careful selection of materials and by controlling the environment though this phenomenon itself can not be avoided. Consequently, the problem of ascertaining the conditions of corrosion under a certain environment, is extremely important in any evaluation of the anti-corrosive properties of the plant materials.

This also applies in the case of the MSF plant, whereby the precise conditions of corrosion should be determined first, so that suitable anti-corrosive materials can be selected. For this purpose, it is necessary to establish what equipment to use and a process for evaluating the results obtained. Thus, this research will focus on investigating the current levels of evaluation test facilities of anti-corrosive properties required for devising an R&D plan for anti-corrosive materials associated with the SWCC sea water desalination, which was mapped out in the related research paper M-2 and on investigating and planning the installation of evaluation test facilities of anti-corrosive properties which SWCC should prepare from now.

2. Methods

At present, the most widely recognized data bases are JOIS, in Japan and DIALOG, in the USA and these will be used as the main source of information.

Consequently, we aim to obtain references in lines with the above mentioned objective by various key words and by combining these from amongst an expanding information system (JOIS has approx. 7,000,000 items and DIALOG has more than 10,000,000 items) which have been stored in these data bases. At the same time, for some of the experiments, there has been no input but valuable data can be found in various PR data which have been published by various material manufactures, and if uncovered, will also be given attention to.

3. Results

3.1 Current Status of Test Equipment Including Corrosion and Electrochemical Test Equipment and Various Analyzers for Evaluating Corrosion Resistance of Materials for MSF Seawater Desalination Plants.

MSF seawater desalting plants handle high-temperature fluid/quiescent seawater, and therefore, evaluation of the corrosion resistance of applied materials, especially metallic materials, is considered one of the most important problems. In evaluating material life and selecting the proper material, suitable corrosion test equipment is used depending on the application purposes for evaluation of corrosion resistance, and corrosion modes and corrosion developing speed which may constitute problems, must be accurately determined. In this investigation, the corrosion test equipment is generally grouped as follows:

- (1) Laboratory-level basic test equipment.
- (2) Monitoring equipment to trace corrosion developing conditions in a laboratory or on the production line.
- (3) Large-scale test equipment on the production line, with the current technical level summarized by a literature search with special emphasis on corrosion test equipment which is desired for installation in SWCC in the future, is proposed.

In the literature search, stress was placed on literature which has been recently published in Japan for data collection and arrangement.

3.1.1 Test Equipment on Laboratory Level

The variety of corrosion test equipment on the laboratory level which basically evaluates the corrosion resistance of materials is immense and it is not our intention here to explain these systems one by one. If any such need exists, technical books should be consulted. This section briefly summarizes the current level of typical test equipment and precautions during operation, with special emphasis on the following points which is believed to be necessary in evaluating the corrosion resistance of materials for MSF seawater desalting plants.

- (1) Immersion type corrosion test
- (2) Alternate immersion test
- (3) Corrosion test accompanied by mechanical action
- (4) Stress corrosion cracking test
- (5) Corrosion test under heat transfer

(1) Immersion Type Corrosion Test¹⁻⁴

a) Total Immersion Test

Any specimen shape is acceptable but a flat plate is selected in view of reproducibility of data, ease of fabrication, and weight loss measurement. In general, about 30 x 30 x t mm or 20 x 40 x t mm specimens are convenient. Where pitting corrosion is a problem, the size of the specimen becomes particularly important and as the area increases, deeper pitting corrosion tends to occur (size effect). For test conditions, temperature, flow rate, and air permeability constitute important factors. To set these factors, thermostats, mantle heaters, magnetic stirrers, gas blow-in, and other general chemical experimental techniques can be applied. When the temperature is high, circulation condensers are installed. Figure 3.1.1 shows a typical design example. In Figure 3.1.1 (a), a stand-by hole is provided in addition to a liquid-phase measurement port, atmospheric gas blow-in port, and circulation condenser. The specimen location can be varied depending on the purpose, such as in the liquid, at the gas-liquid interface, or in the gas. When continuous tests are carried out to determine corrosion under boiling conditions, it is recommended that detectors for cooling water pressure, water temperature, etc. be installed to achieve automatic maintenance and control. Figure 3.1.2 shows an example to automatically turn off the heating power supply when cooling water pressure lowers. The amount of test solution should be determined by considering the effect of changes in the solution, due to consumption of corrosive substances or accumulation of corrosion products, on the subsequent corrosion, and should be renewed at specified intervals, or continuously injected or circulated using a fixed-rate pump on an as-required basis. However, excessive renewal of the solution should be avoided. The ratio of solution volume to specimen surface area is pertinent to the specimen area and should be 20-40 ml/cm². One type of specimen should be used for one test vessel as much as possible. Immersing several types of dissimilar metals in the same container may cause corrosion products to affect the corrosion rates of other specimens. For example, corrosion products of copper decrease the corrosion rate of titanium and stainless steel and accelerate that of aluminum. Specimens should be insulated physically and electrically from one another. In tests which tend to cause crevice corrosion, special attention must be shown concerning the specimen holding method. Ceramic, glass, or fluororesin is usually used for the holder material.

The test period constitutes an important problem. Like the corrosion of iron in an acidic solution, if a corrosion rate is constant in terms of time, corrosion property can be evaluated by a short-time test, but in general, the corrosion rate varies with time due to the formation of surface film and the adhesion of corrosion products. For example, lead in sulfuric acid corrodes violently at the initial stage, but thereafter forms a protective film. When specimens are set for tests, it is essential to accurately determine the relationship between plating thickness and plating life. When the protection capability of the formed layer is lost, lead abruptly and dramatically cor-

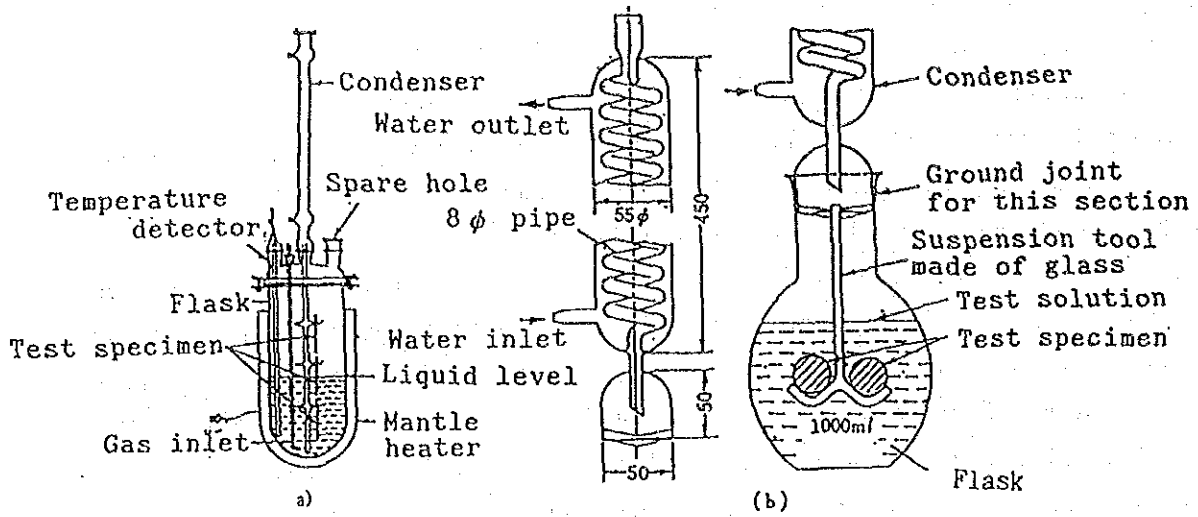


Fig.3.1.1 Immersion type testing apparatus'

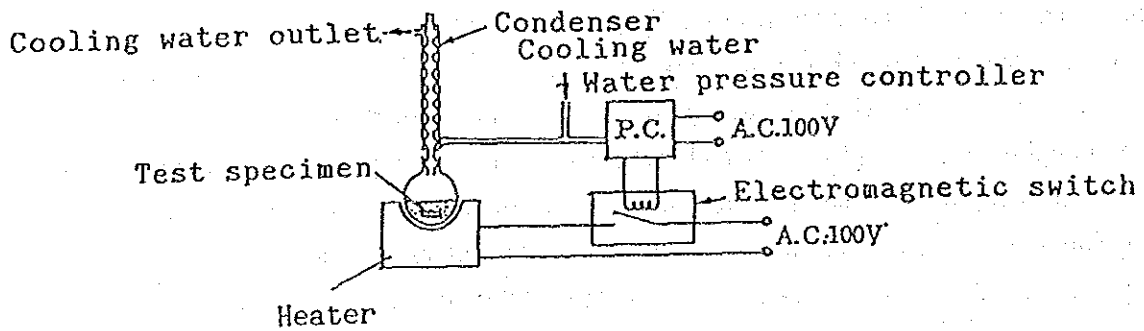


Fig.3.1.2 Automatic control method using cooling water pressure'

rodes. The general test period is about 48–168 hours when a sufficient weight loss is achieved against the balance sensitivity. A method to easily judge the change with time was published by Wachter and Treseder. It is called the "planned interval test" and the procedure and evaluation method for the results are shown in Table 3.1.1.

Upon completion of tests, specimens are washed and the corrosion rate is determined, but before washing, the external appearance should be observed and recorded. This will help in evaluating localized corrosion such as pitting and concentrated cell corrosion. The washing procedure varies in accord with the adhesiveness of corrosion products, but the products are removed by mechanical, chemical, or electrochemical techniques. Whichever technique is selected, the effect on the base metal must be investigated in advance using blanks, or the change of weight loss with time must be determined. Figure 3.1.3 is an example in which true corrosion loss is found from the weight change with respect to washing time. Table 3.1.2 shows a method to remove the corrosion products of various metals and alloys after tests.

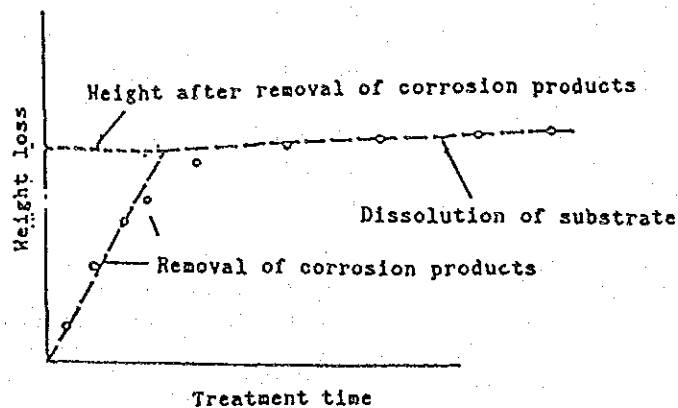
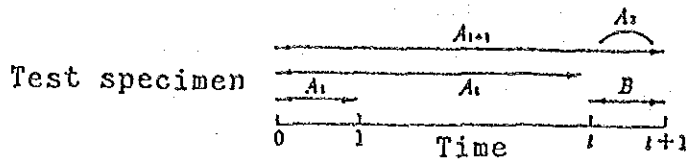


Fig.3.1.3 Method to find weight loss by corrosion¹

Evaluated results are expressed as weight loss (corrosion rate: $\text{g/m}^2/\text{h}$, mdd [$\text{md}/\text{dm}^2/\text{day}$]) or penetration (corrosion rate: mm/y , ipy [inch/y]). Table 3.1.3 shows the conversion table of the corrosion rate. In general, corrosion speed varies with time and causes errors in extrapolating annual corrosion rates from tests carried out only for one week or so.

The test period should be mentioned. In the case of general corrosion only, this type of

Table 3.1.1 Planned interval test method¹



Place the same type of specimen in the same corrosive solution. Hold the specified test conditions constant for complete $t + 1$ hours. A_1 , A_i , A_{i+1} , B represent the degree of corrosion of each specimen subject to corrosion, and A_2 is found by subtracting A_i from A_{i+1} .

Condition generated during corrosion test		Judgment
Corrosiveness of the solution	No change	$A_1 = B$
	Reduced	$B < A_1$
	Increased	$A_1 < B$
Corrosiveness of the metallic material	No change	$A_2 = B$
	Reduced	$A_2 < B$
	Increased	$B < A_2$

Combination of conditions		Judgment
Corrosiveness of the solution	Corrosiveness of the metallic material	
1) No change	No change	$A_1 = A_2 = B$
2) No change	Reduced	$A_2 < A_1 = B$
3) No change	Increased	$A_1 = B < A_2$
4) Reduced	No change	$A_2 = B < A_1$
5) Reduced	Reduced	$A_2 < B < A_1$
6) Reduced	Increased	$A_1 > B < A_2$
7) Increased	No change	$A_1 < A_2 = B$
8) Increased	Reduced	$A_1 < B > A_2$
9) Increased	Increased	$A_1 < B < A_2$

Example of planned interval test method

Conditions: Inject dry HCl gas by atmosphere into 200 mL of a mixture comprising 10%AlCl₃ and 90%SbCl₃ and immerse two pieces of low carbon steel specimens of 314 x 3 inches at 90° C.

Intervals [day]	Weight loss [mg]	Corrosion [mil]	Apparent corrosion rate [mil/yr]
A_1 0-1	1080	1.69	620
A_i 0-3	1430	2.24	270
A_{i+1} 0-4	1460	2.29	210
B 3-4	70	0.11	40
A_2 calculated 3-4	30	0.05	18

$$A_2 < B < A_1$$

$$0.05 < 0.11 < 1.69$$

Consequently, during corrosion test, corrosiveness of the solution markedly decreases, indicating that localized protective film has been formed on the steel surface.

Table. 3. 1. 2 Method to remove corrosion products.

Material	Chemicals	Time	Temperature	Remarks
Aluminum and aluminum alloys	70% HNO ₃	2~3 min	Ambient temperature	Thereafter rub lightly
	or 2% CrO ₃ , 5% H ₃ PO ₄ solution	10 min	175~185° F (79~85° C)	Use when oxide film is unable to remove with HNO ₃ treatment. Thereafter, treat with 70% HNO ₃ .
Copper and Copper alloys	15~20% HCl	2~3 min	Ambient temperature	Thereafter rub lightly
	or 5~10% H ₂ SO ₄	2~3 min	Ambient temperature	Thereafter rub lightly
Lead and lead alloys	1% acetic acid	10 min	Boiling	Thereafter rub lightly. Remove PbO.
	or 5% ammonium acetate	5 min	High temperature	Thereafter rub lightly. Remove PbO, PbSO ₄ .
	80g/L NaOH, 50g/L MANIOL, 0.62g/L hydrazine sulfate	30 min or until clean	Boiling	Thereafter rub lightly
Iron and Steel	20% NaOH, 200g/L Zinc powder	5 min	Boiling	---
	or Concentrated hydrogen chloric acid 50g/L SnCl ₂ + 20g/L SbCl ₃	until clean	Low temperature	---
Magnesium and magnesium alloys	15% CrO ₃ , 1% AgCrO ₃ solution	15 min	Boiling	---
Nickel and nickel alloys	15 - 20% HCl	until clean	Ambient temperature	---
	or 10% H ₂ SO ₄	until clean	Ambient temperature	---
Stainless steel	10% HNO ₃	until clean	140° F (60° C)	Avoid entry of chloride
Tin and tin alloys	15% Na ₃ PO ₄	10 min	Boiling	Thereafter rub lightly
Zinc	10% NaH ₂ Cl, then 5% CrO ₃ , 1% AgNO ₃ solution	5 min 20 sec	Ambient temperature Boiling	Thereafter rub lightly ---
	or saturated ammonium acetate	until clean	Ambient temperature	Thereafter rub lightly
	or 100g/L NaOH	15 min	Ambient temperature	---

expression is acceptable, but when localized corrosion is considered, it becomes necessary to investigate the profile, distribution, and depth of pitting as well as other factors. It is difficult to accurately express the degree of pitting, but expression methods used by Champion, Henke, and the American Petroleum Institute are available. Table 3.1.4 shows a method to express pitting advocated by Henke. When intergranular corrosion and corrosion due to metallurgical factors are concerned, microscopic observation is effective.

b) Partial Immersion Test

The wall of a metal vessel has many chances to come in contact with both liquid and gas and may cause abnormal corrosion at the interface. Therefore, it is necessary to carry out corrosion tests under a partially immersed condition. In particular, aluminum alloys frequently generate this kind of marked waterline corrosion, to which special care must be taken. When partial immersion is expected for a comparatively long period, the waterline lowers due to the evaporation of water. F. A. Champion replenished the vessel with water by a device illustrated in Figure 3.1.4 and held the water level to an accuracy of +0.1 mm. When waterline corrosion is comparatively severe, the specimen should be positioned in such a manner that its center portion is located at the water line.

Maintaining the water line as accurately as possible to concentrate corrosion, and measuring a decrease in high tension can clearly show the degree of this kind of corrosion.

(2) Alternate Immersion Test (Cyclic Dry and Wet Test)^{2,4}

The environment in which the metal surface is repeatedly immersed and dried can be frequently and practically observed. The alternate immersion test reproduces this condition fairly accurately. This test method can sometimes be used to accelerate corrosion by a solution, since cyclic immersion and drying allows oxygen and carbon dioxide to act strongly on the metal. This method is also used to detect the corrosion of metal coatings anodic to base metal. This type of coating effectively prevents corrosion when the surface is covered with an electrolytic solution even if a pinhole exists, but during the drying process, corrosion tends to develop at the pinhole, and the difference can be determined quickly (ex. inspection of galvanized steel: ammonium chloride solution is used with 1 cycle for 15 minutes and an immersion time of 20 sec.).

What matters most in this test method is how to determine the immersion time and drying period. The ratio of the two and the time designated for one cycle vary greatly from one researcher to another. As an example, the ASTM regulation for nonmetal is shown in Table 3.1.5. A is the case when the drying period is short and corrosion of specimens is accelerated, and B is the case when the drying period is long and corrosion is retarded. In short, it is practically

Table 3.1.3 Conversion table of corrosion rate unit¹

D: specific gravity A x f = B
 f: numerical value in the table

A \ B	Corrosion rate				Penetration rate		
	g/m ² ·h	g/m ² ·day	mdd	g/m ² ·year	mm/year	ipy	ipm
g/m ² ·h	1	24	240	8760	8.76/D	0.345/D	0.0287/D
g/m ² ·day	0.0417	1	10,	365	0.365/D	0.0144/D	0.0012/D
mdd	0.00417	0.1	1	36.5	0.0365/D	0.00144/D	0.00012/D
g/m ² ·year	0.000114	0.00274	0.0274	1	0.001/D	0.0000394/D	0.00000328/D
mm/year	0.114D	2.74D	27.4D	1000D	1	0.0394	0.00328
ipy	2.90D	69.6D	696D	25400D	25.4	1	0.0832
ipm	34.8D	835D	8350D	305000D	305	12	1

Table 3.1.4 Indication method of pitting by Henke¹

Item	Symbol	Method of presentation	Representation example 84S152101
Pitting depth	AAA	Pitting depth/original plate thickness [%]	<u>84</u> : Pitting depth reaches up to AA 84% of the original plate thickness.
Profile of pitting wall	B	Steep or Gradual [%]	<u>S</u> : Pitting wall gradient is steep. S/G
Pitting Area	CC	Pitting area/overall sample area [%]	<u>15</u> : Pitting occurs 15% of the overall surface area. CC
Growth rate	DD	Pitting depth per year/original plate thickness [%]	<u>21</u> : Pitting increases depth by 21% of the original plate thickness in one year. DD
Pitting size	EE	Ranked in accord with reference material 01~09	<u>01</u> : Size 01 class EE 84/21=4 (duration of years)

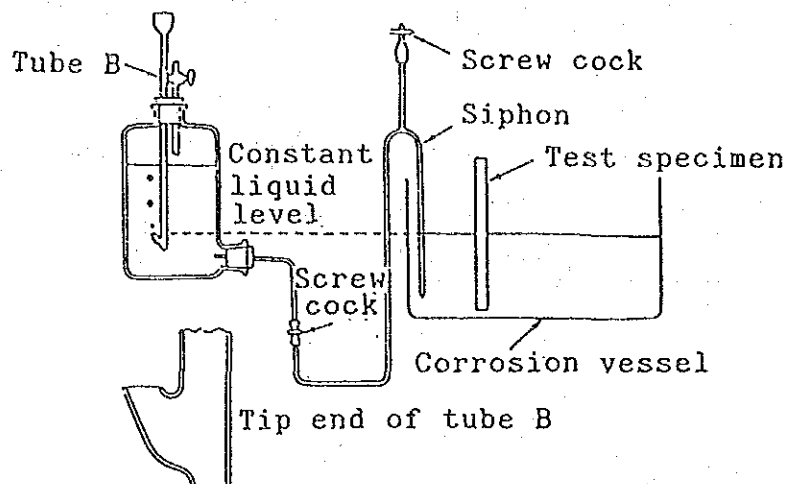


Fig.3.1.4 Method to hold liquid level in partial immersion test²

Table 3.1.5 ASTM regulation for nonferrous metals²

	1 cycle	Immersion	Drying
A	1~3 min	0.5 min	0.5~2.5 min
B	3~6 min	1~2 min	2~4 min

impossible to exactly reproduce actual conditions no matter how intensively these cycles are studied. Therefore, since it is enough for the test to have significance as a kind of comparison test or acceleration test, it is considered desirable to emphasize reproducibility of the results. Conventional studies have indicated that temperature and humidity above the liquid have great effects on reproducibility. The utilization of radiation heat to promote specimen drying is sometimes used, but the complications involved may also have a detrimental effect on reproducibility, to which care must be taken (it is difficult to reproduce completely identical conditions in other laboratories).

As an alternate immersion method, there is a method to move the liquid vertically (to achieve this, there are two methods; one to lower and raise the liquid level only and the other to lower and raise the liquid together with the container), but in general, it is more common to move the specimens vertically. The method illustrated in Figure 3.1.5 is the easiest method for moving specimens vertically, but in general, methods to install specimens to a jig in the form of a rotating wheel or to move specimens with a crank, cam, or a geared motor are popularly used. In any case, the lower portion of a specimen is immersed in liquid longer than the upper portion and during the drying period, residue liquid is concentrated on the lower portion, which dries more slowly and is more susceptible to corrosion. Consequently, this fact must be taken into account in evaluating the results.

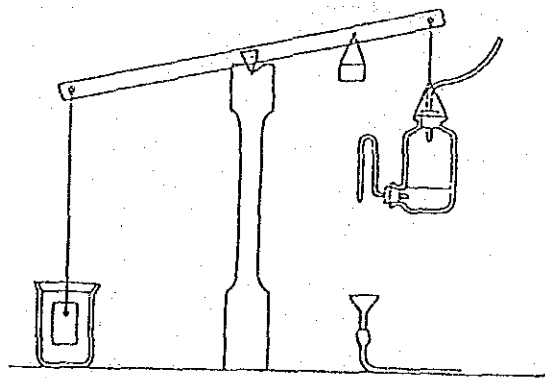


Fig.3.1.5 Simple alternate immersion method²
(F. Bainbridge)

(3) Corrosion Test under Mechanical Action⁵⁻¹⁹

This section does not focus on the corrosion test under simple fluid circumstances but rather describes a technique in which protective film on the metal surface is destroyed and removed by mechanical action such as the impingement of liquid or friction, and corrosion is accelerated, that is, an erosion corrosion test method. The Erosion Corrosion Test Method Sectional Committee of the Japan Society of Corrosion Engineering investigated erosion corrosion test methods and identified that test methods fall into five broad categories according to the motion of fluid and specimens: rotating, stirring, jet, vibration, and loop (circulating flow) types.

The remainder of this section discusses test methods related to erosion and corrosion as well as erosion accompanied by corrosion. In either case, results are expressed as a relationship between damage rate (weight or volume loss) and test time.

a) Flow Rate Test (Erosion Corrosion Test)

1) Droplets and Liquid jets

This is a damage test by impingement of liquid jets and is standardized as "Liquid Impingement Erosion Testing" by ASTM G73-82, but in the high speed region of 50 m/s-1000 m/s impingement speed, this is an erosion test rather than an erosion/corrosion test. Figure 3.1.6

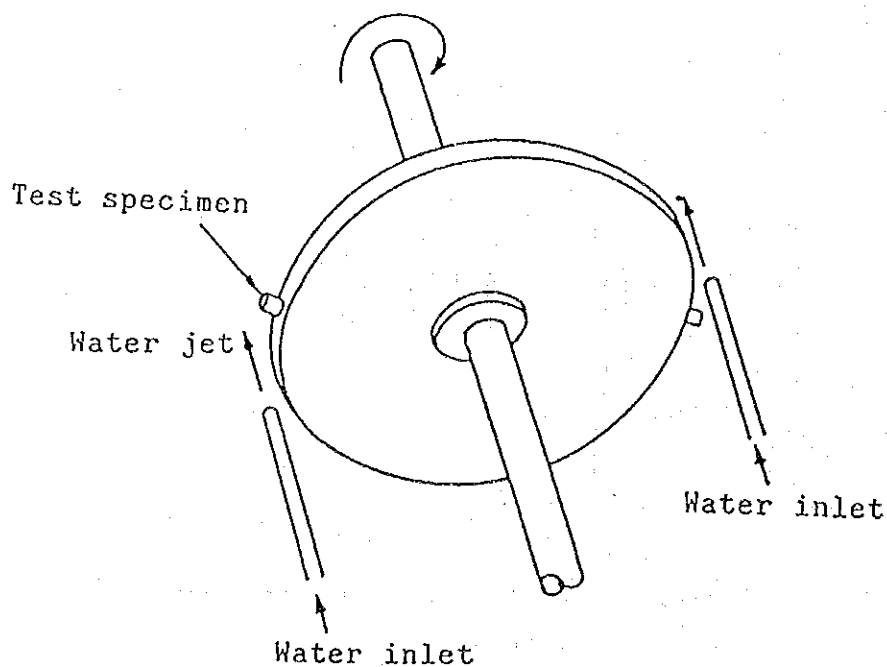


Fig.3.1.6 Rotating disc type liquid jet impact testing apparatus ⁵

shows an example of rotating disc type test equipment. Specimens installed around a rotating disc are designed to be subjected to impact repeatedly by cutting liquid (water) jets flowing out from round nozzle holes (0.1–5 mm) and specimens with either curved (aerofoil and cylindrical) or flat surfaces are used depending of the test priorities.

In the erosion corrosion tests conducted at a flow rate of 20 m/s or lower, a loop type test apparatus which is located in a conduit is used and in this occasion electrochemical measurement is also carried out.

2) Solid–liquid System

An erosion corrosion test method is shown for a system, such as for slurry containing solid particles in the liquid. In this system, rotating, stirring, jet, and loop type test methods are used.

(1) Rotating type

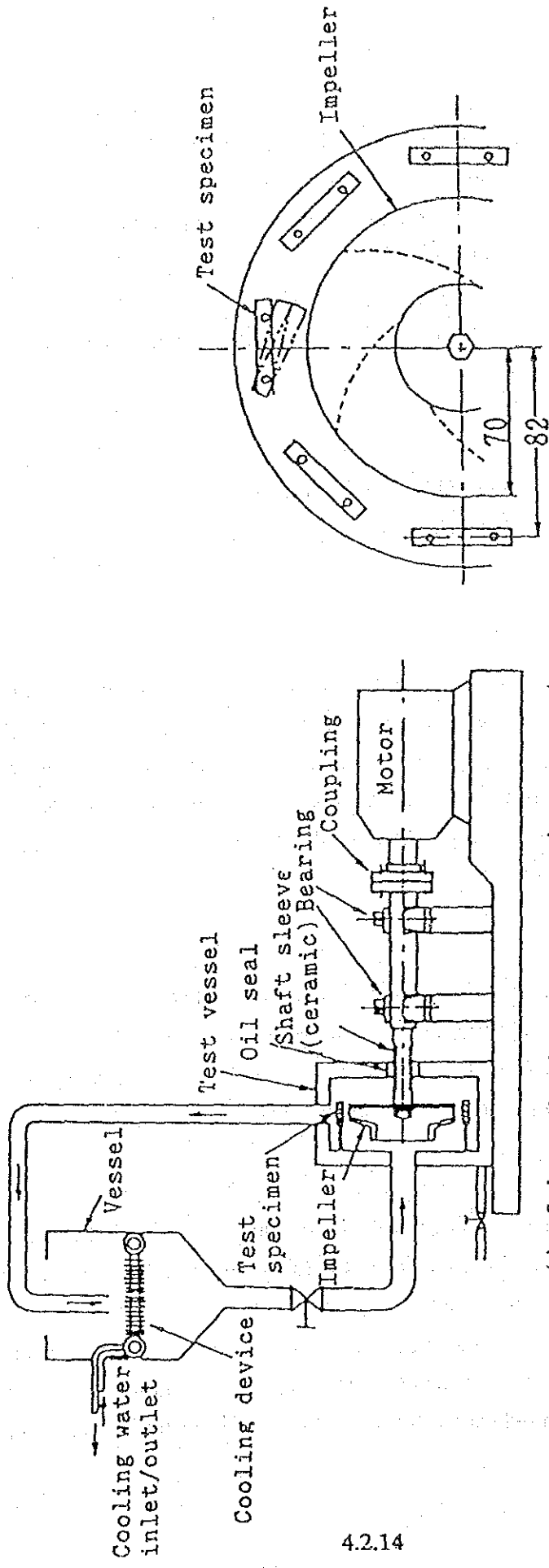
This is a system in which specimens rotate in the slurry and is available in two types; vertical and horizontal. In a vertical type testing device, a cylindrical specimen (6 x 30 mm) is rotated by an electromagnetic induction system with no seal provided. For a drum type test device, specimens are installed to a drum wall or a rotor, and the wall and the rotor are rotated or both are counter–rotated to each other. Many specimens can be installed at one time but the complicated flow conditions constitute a problem.

(2) Stirring type

Specimens are fixed in a vessel and slurry is allowed to flow by the use of a stirrer. A plurality of strip specimens are held vertically in the vessel and a stirrer is rotated to let slurry impinge on the specimens. Experimental conditions, such as flow rate, temperature, and specimen setting angle, can be controlled and electrochemical measurement is possible.

(3) Jet type

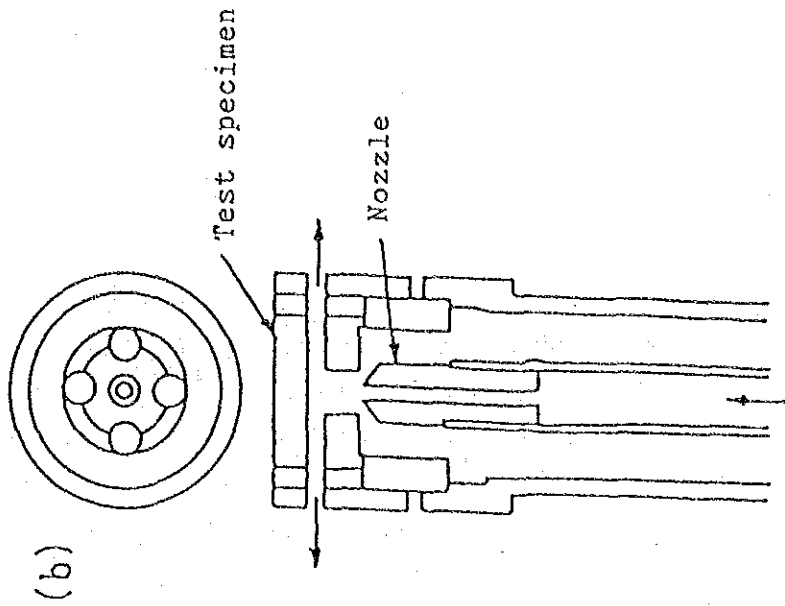
This system allows slurry jets to impinge on specimens. Figure 3.1.7 shows a test apparatus designed and fabricated by the Erosion Corrosion test method sectional committee, which uses a jet stream from pump impellers to impinge on a plurality of specimens, and control of experimental conditions and electrochemical measurement are enabled. This is recommended as a quick test method to select material. Figure 3.1.8 shows a slotted jet test device. In this device, only the supernatant is circulated, which has the advantage of eliminating damage to pumps.



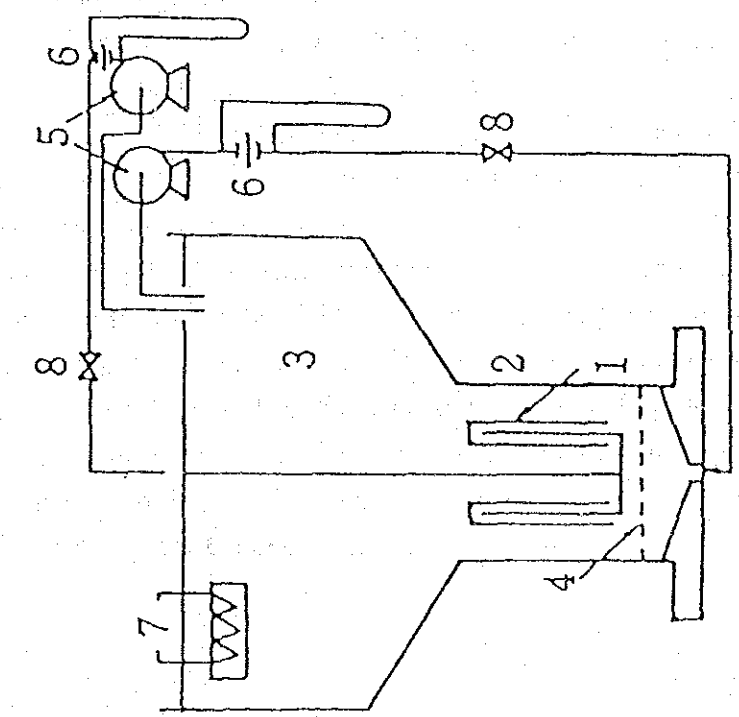
(a) Schematic drawing of testing apparatus

(b) Testing section

Fig.3.1.7 Jet type erosion-corrosion testing apparatus



(b)



(a)

- 1. Testing section
- 2. Fluidized bed
- 3. Precipitator
- 4. Distributor
- 5. Pump
- 6. Venturi
- 7. Heater
- 8. Valve

Fig.3.1.8 Schematic diagram (a) and testing section (b) of gap jet type erosion-corrosion testing apparatus⁵

(4) Loop type

The jet type belongs to the loop type, but there is a type which circulates slurry in the loop type conduit by the use of a pump (figure 3.1.9). Either a straight pipe or a bend in part of the conduit is used as a test portion or specimens are inserted in the conduit. It is possible to control experimental conditions as well as carry out electrochemical measurement. Since the loop type is designed to obtain data for simulation with actual equipment or for equipment design, in general, it is larger and uses more liquid than types (1) through (3).

b) Cavitation Erosion Test

The most significant factor in erosion is cavitation erosion, in which sudden change occurs in the pressure of a rapidly moving metal surface and air bubbles are formed and collapse where pressure is high. Under such condition, the impact pressure generated when this condition is repeated rapidly results in damage. This can be called gas-liquid system erosion. When corrosion is involved, it is called cavitation erosion corrosion. Examples of the cavitation erosion test method include the following:

1) Venturi Tube Method

The venturi tube method has been popularly employed for various tests. Figure 3.1.10 shows the venturi tube type cavitation test section, which can investigate damage in specimens installed to the position of turbulence generated when a high-speed stream passes a locally narrow passage. In the water tunnel method, spherical or cylindrical specimens are inserted into the center to generate and dissipate cavitation air bubbles. The above-mentioned loop type method using high-speed liquid is complicated in operation and requires a long time for testing but has the advantage of enabling the experimental conditions to be easily set, rendering itself suitable for studies of cavitation erosion corrosion. This is used for various studies on erosion by flowing sea water in valve pumps, piping materials, and ships, as well as for studies on corrosion-protection.

2) Rotating Disc Method

As shown in Figure 3.1.11, specimens are installed to a disc and rotated at high speed in a hermetically sealed liquid tank. The test apparatus is simple and a large number of specimens can be installed at one time. Since relative speed is identified, the relation with actual conditions can be taken into account, but electrochemical measurement is difficult due to the rotating motion.

3) Vibration Method

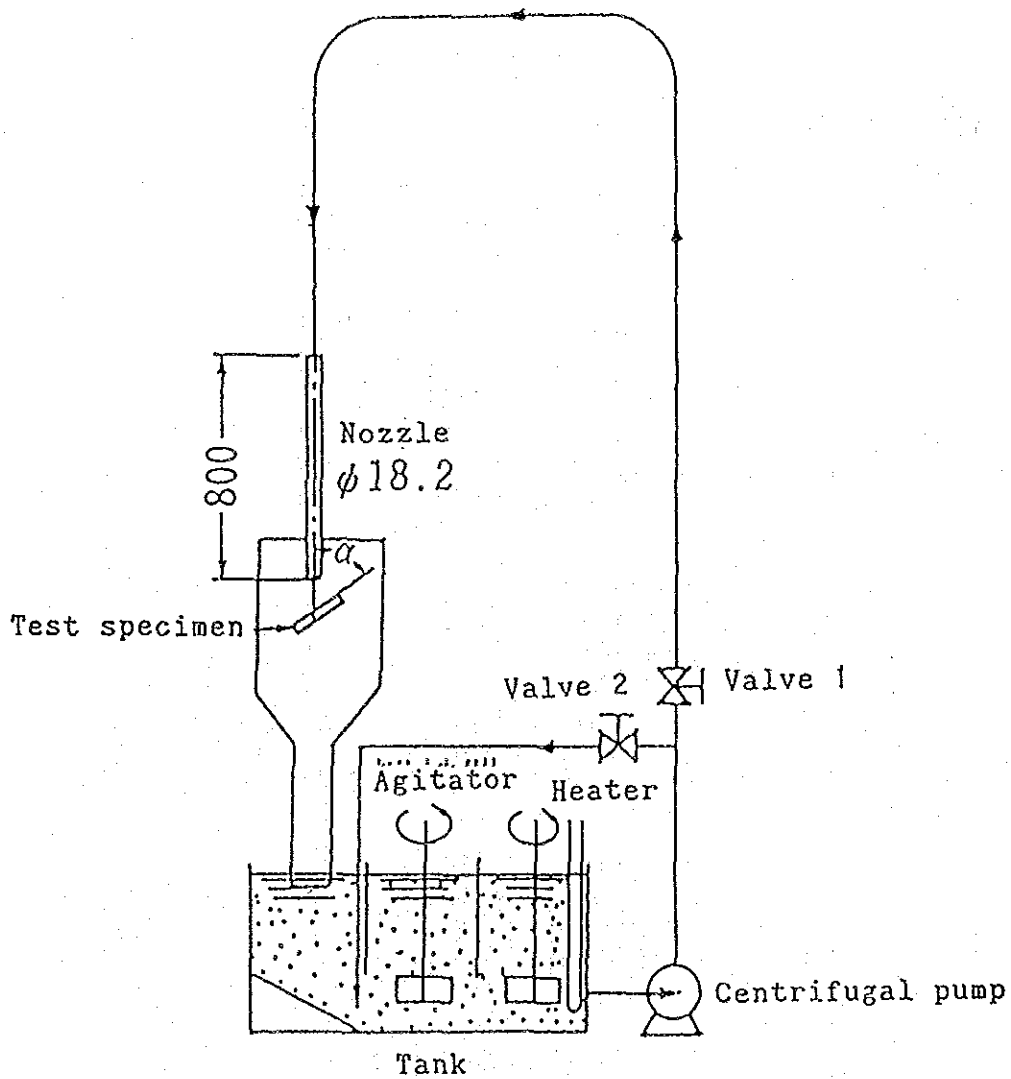


Fig.3.1.9 Jet/loop type slurry erosion-corrosion testing apparatus⁵

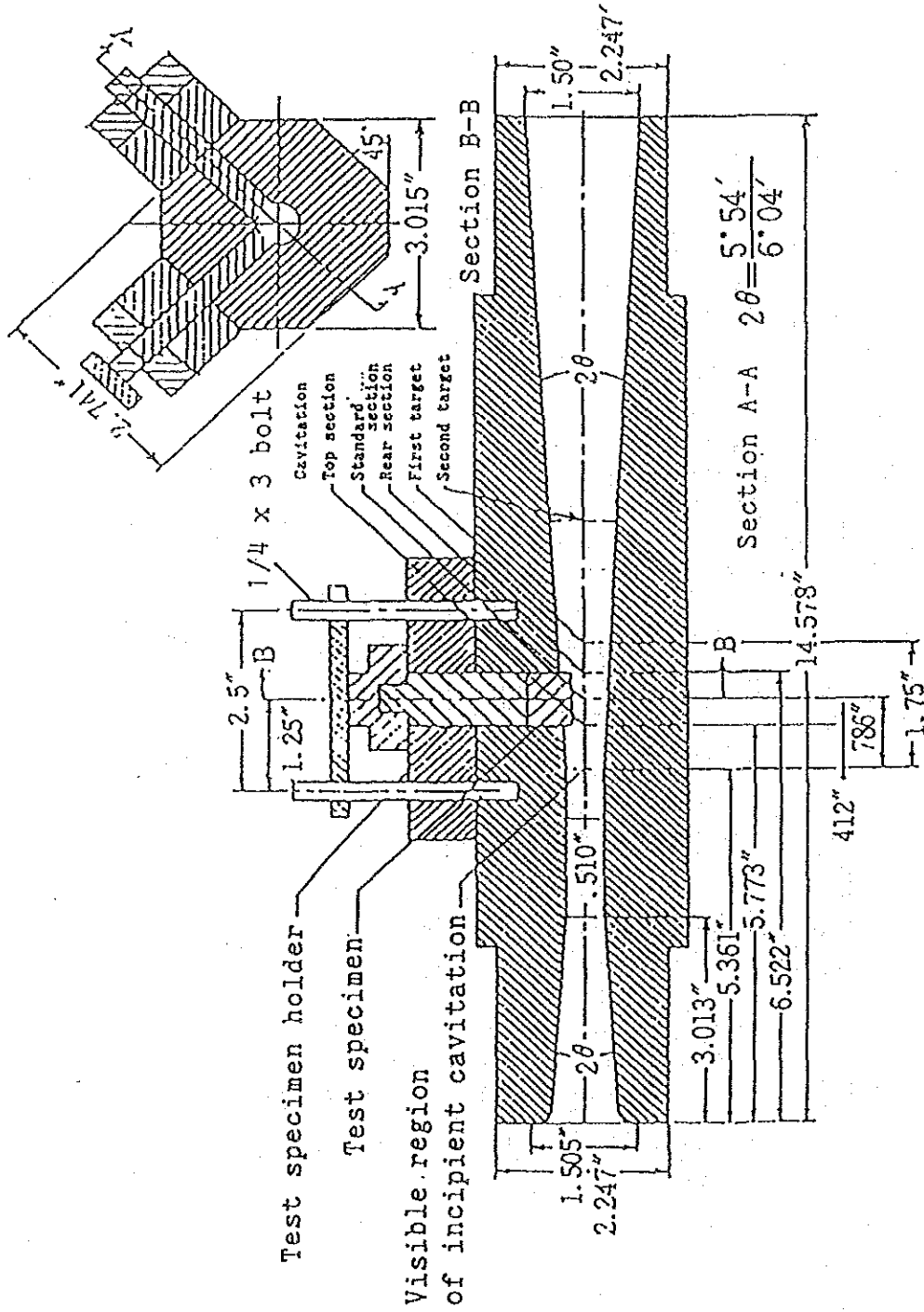


Fig.3.1.10 Venturi tube type cavitation test section²⁰

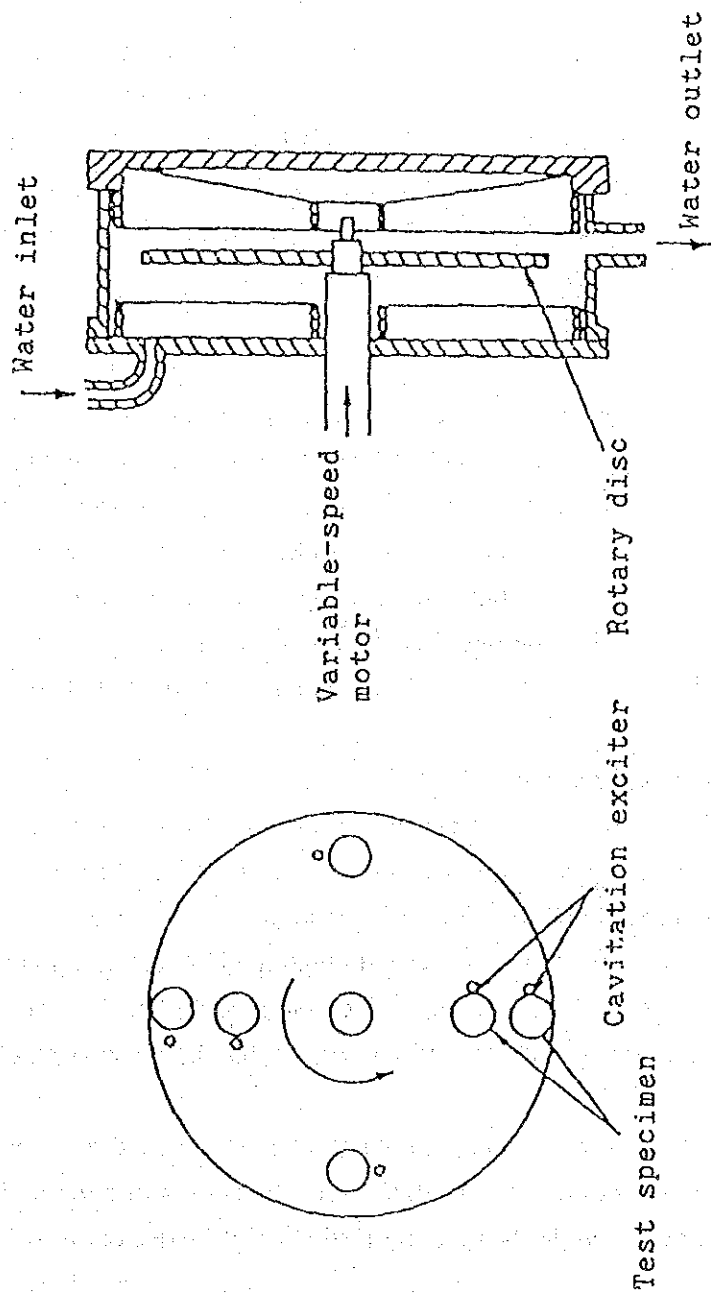


Fig.3.1.11 Rotating disc method (gas-liquid system) ⁵

The vibration method has most popularly been employed as a rapid test method for the selection of anti-erosion materials and is standardized by ASTM G 32-77 (Standard Method of Vibratory Cavitation Erosion Test). Figure 3.1.12 shows a magnetostrictive test apparatus. A nickel tube is vibrated at high frequency by magnetostrictive effects and this vibration is transmitted to specimens in contact with the liquid via a horn, causing air bubble generation and collapse to be repeated on the lower surface of the specimens, resulting in damage. It has advantages of short test time, small specimens, and requiring a small amount of test solution. However, it is unsuitable for a mock-up test because experimental conditions are difficult to change and the relation of flow rates, etc. between test conditions and actual conditions is not sufficiently clear, and it therefore should be used as a comparison test for materials.

4) Jet Method

The jet method provides a jet from nozzles parallel to the rotating shaft with respect to a rotating specimen, as shown in Figure 3.1.13, and the liquid impinges on the specimen at a speed relative to the circumferential speed of the specimen and that of the jet. The specimen is subjected to the jet impingement upon every rotation, causing sudden pressure changes and generating cavities. It has the advantage that a large number of small-size specimens can be tested simultaneously, and since the relative speed to the liquid is identified, the similarity can be checked. It is also popularly used for comparison tests of materials, similarly to that of Method ³.

(4) Stress Corrosion Cracking Test Method²⁰⁻²⁶

When metallic materials are placed in a specific corrosive environment with tensile stress loaded, cracking may occur in a crystal grain or along grain boundaries. In general, it takes a long time to recognize the occurrence of stress corrosion cracking under a practical environment, but as a test method, it is a common practice to generate high-level stress and produce a severe environment for acceleration testing. There is a specified combination between the metal which can generate stress corrosion cracking and the environment. Table 3.1.6 shows an example of a test solution.

For the stress application method, there is a constant strain method and a constant load method, as well as that belonging to the intermediate. The constant strain method carries out tests in the elastic or plastic range, while the constant load method carries out tests in the elastic range.

1) Constant Load Method

In the constant load method, a specified stress is easy to provide and the rupture time can be accurately determined, but in general, a large-size apparatus is required and it is necessary to

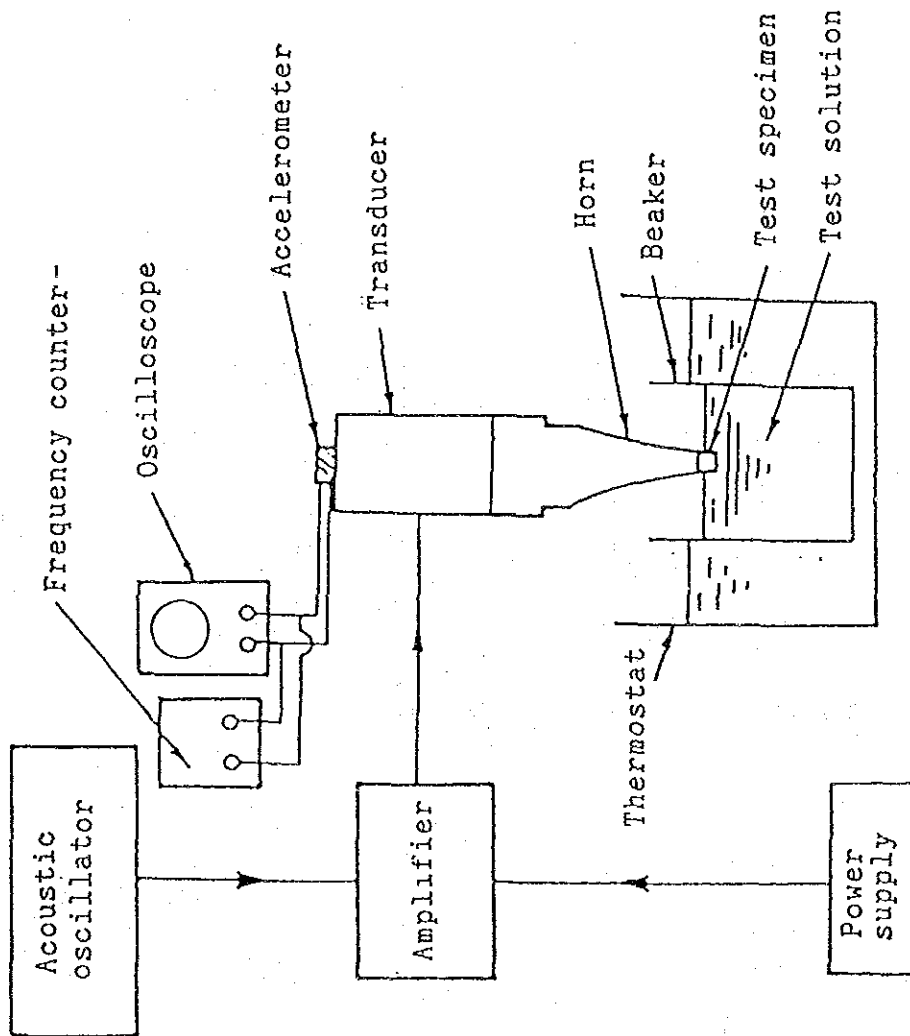


Fig.3.1.12 Magnetostrictive type cavitation erosion testing apparatus⁵

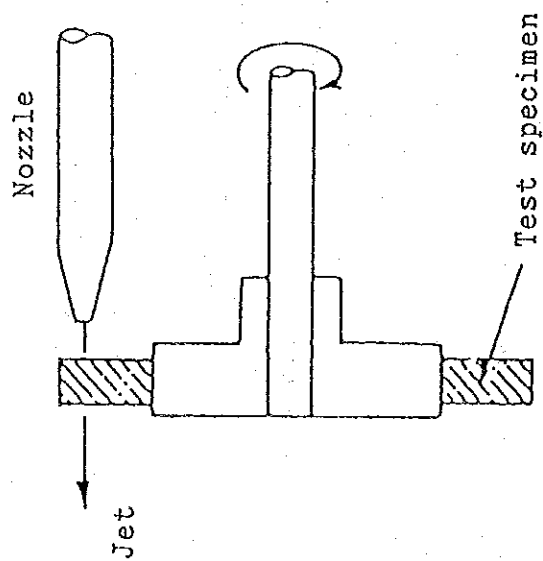


Fig.3.1.13 Jet method²

Table 3.1.6 Stress corrosion cracking test solution

Material	Investigated components	Test solution
Austenitic stainless steel	Cl ⁻	<ol style="list-style-type: none"> 1) 60%CaCl₂+0.1%HgCl₂⁵²⁾ 2) 42%MgCl₂⁵⁹⁾ 3) 6%NaCl+1.5%Na₂Cr₂O₇⁶⁰⁾ 4) 0.5NNaCl+0.1NNaNO₂⁶⁷⁾
Austenitic stainless steel	H ₂ SrO ₆	<ol style="list-style-type: none"> 1) Distilled water + SO₂ gas (4h) + H₂S (3h) ambient temperature (Wackenroder solution)
High-tensile strength steel	Hydrogen	<ol style="list-style-type: none"> 1) H₂S saturated 0.5% CH₃COOH solution 2) Cathodic electrolysis in As₂O₃ saturated dilute sulfuric acid
Carbon steel	NO ₃ ⁻	<ol style="list-style-type: none"> 1) 60%Ca(NO₃)₂ + 3%NH₄NO₃ (boiling)

exercise care when the cross sectional area of a specimen is reduced by corrosion as the test progresses.

<1> Simple tensile type

As shown in Figure 3.1.14, a lever type loading method using a lever is extensively used. Tests are carried out on the specimen installed in a test vessel which can control temperature, pressure electrochemically. This type can identify the stress condition and provide good reproducibility, but the equipment is costly and it is, therefore, not suited for tests which require many tests to be carried out simultaneously.

<2> Plane bending test

This is a cantilever type test method which applies a constant load and plate type specimens with a rectangular cross section are used. In the case of smoothed specimens, the external surface elastic stress can be calculated from the moment the applied load is given.

2) Constant-strain Type Test Method

The constant-strain type test method can be easily carried out by providing a specified strain by fixing specimens to jigs or tightening bolts and nuts, as shown in Figures 3.1.15 and 3.1.16, and placing the specimens in the corrosive environment. This test method has problems, namely, that rupture time is difficult to determine accurately, stress conditions are difficult to identify, and dynamic data are difficult to obtain, but it has advantages that small specimens can be used and many tests can be performed in a short time. Systems in which stress is provided by three-point or four-point support bending have been popularly used and in addition to these, various test methods have been designed depending on the purposes.

Figure 3.1.17 (a) is called the CBB (creviced bent beam) method, which enables reproduction of cracks by generating a crevice from the outside under an environment in which it is difficult to generate stress corrosion cracking from a simple smoothed bending plate surface. This method was developed for stress corrosion cracking tests in high-temperature high-pressure water for nuclear power plants. The CBB (creviced bent beam) technique is an improved, constant strain test method developed in Japan for evaluation of the stress corrosion cracking of stainless steels used in nuclear power plants. It provides a crevice between graphite fiber wool and the test specimen and allows the graphite fiber wool to act as an active site for cathodic reaction (reduction reaction of dissolved oxygen). This has features of markedly accelerated intergranular stress corrosion cracking and good reproducibility.

Figure 3.1.17 (b) is called a double U-bend method, which can generate stress corrosion cracking on the external surface of the inner U-bend plate by crevice effects.

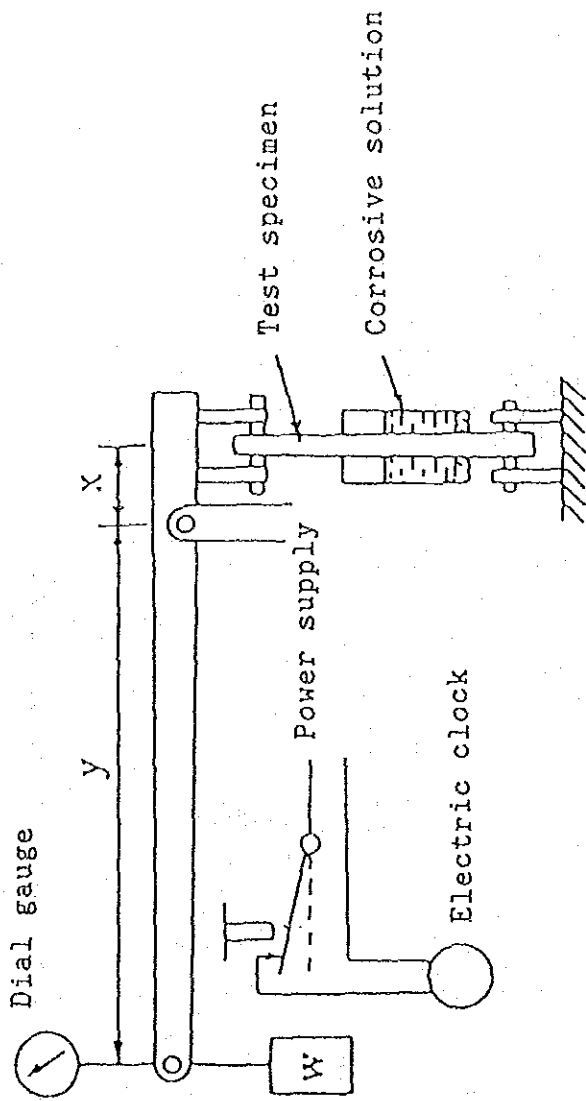
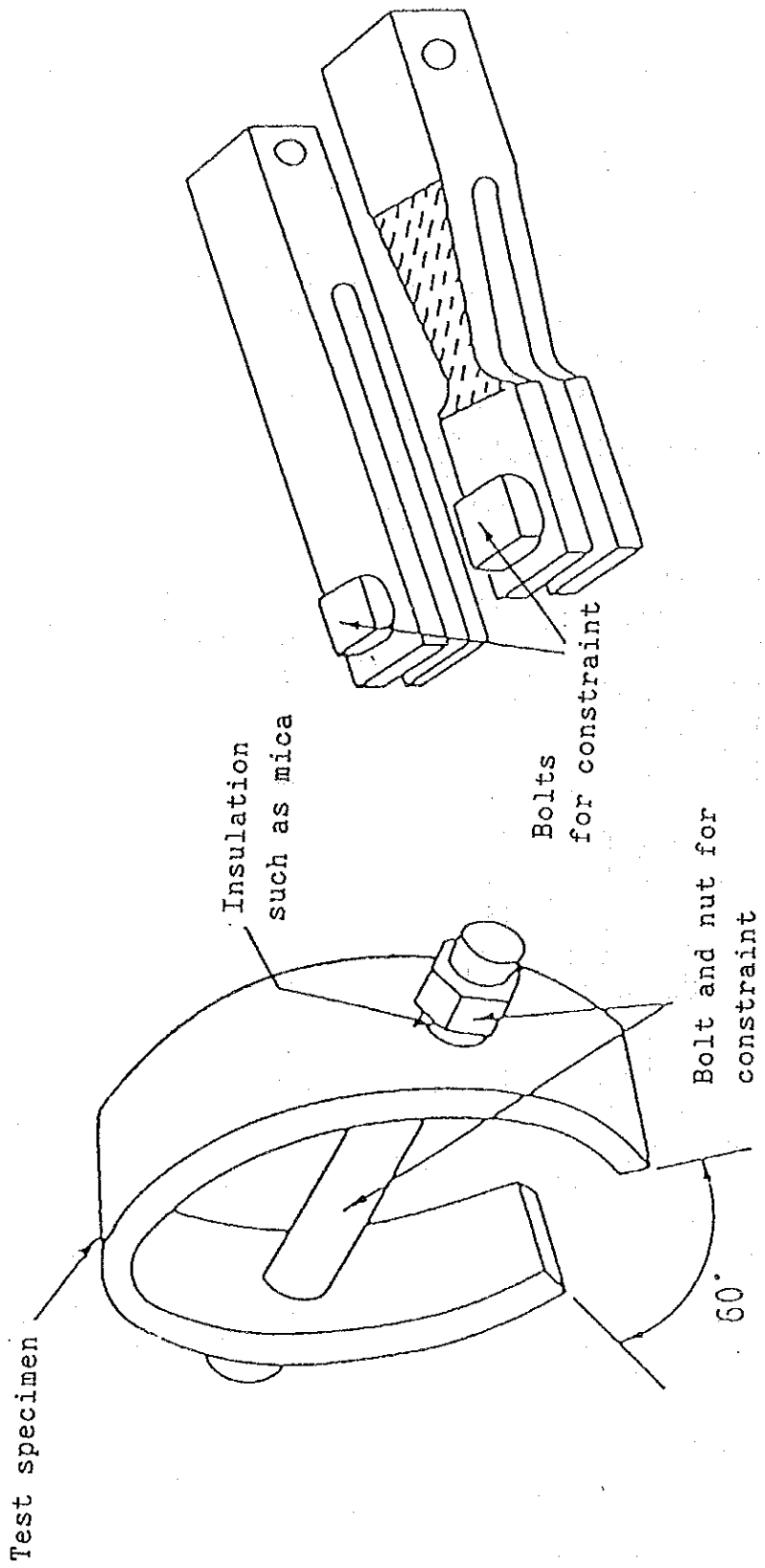


Fig.3.1.14 Lever type constant loading method ?



(a) C-ring specimen (b) Tuning fork type specimen

Fig.3.1.15 Examples of constant strain specimens

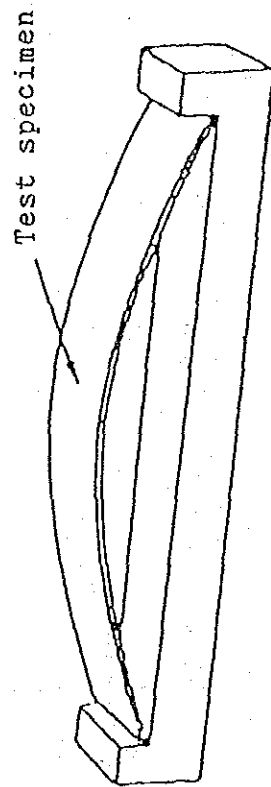
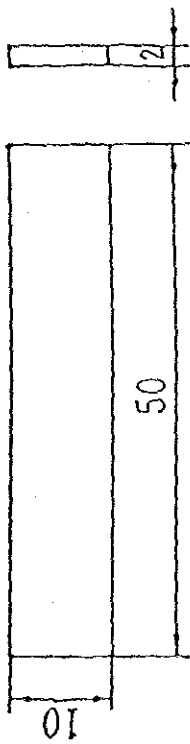
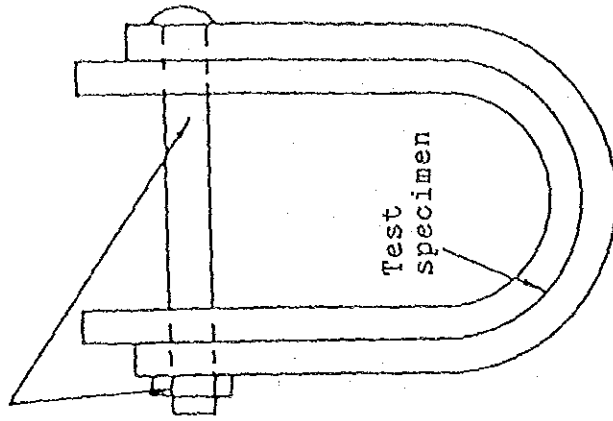


Fig.3.1.16 Jig for holding constant strain²

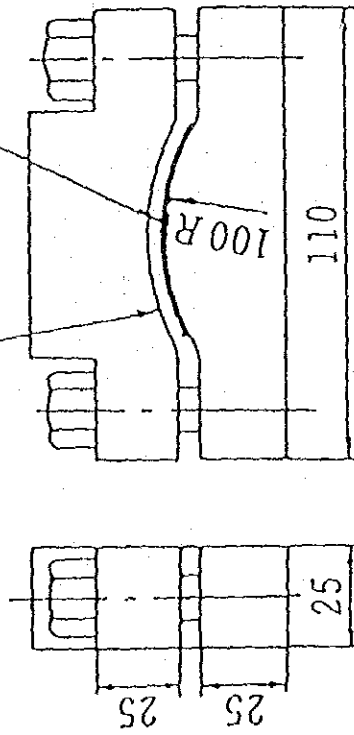


Constraint by bolt and nut



(b) Double U-bend specimen

Graphite Test specimen
fiber wool (50 X 10 X 2)



(unit: mm)

(a) CBB test specimen and test method

Fig.3.1.17 Improved type constant strain specimen to provide crevice effect⁵

Figure 3.1.18 shows an example of the Wicking test method (ASTM C 692) which evaluates stress corrosion cracking from the outer surface under a heat insulation material. The inner surface is heated with a band heater and diluted harmful ions which penetrate the heat insulation material concentrate at the specimen surface to generate stress corrosion cracking. The external surface stress is expressed as a stress resulting from load stresses caused by tightening bolts and nuts and tensile thermal stresses generated by temperature differences in the wall.

To determine stresses by these test methods, stresses must be calculated theoretically from strain rates or converted from stress-strain curves. The calculation formula when a specimen is supported at four points (Figure 3.1.19) is shown as follows:

$$y = (Wa/4Ed^3) \cdot (3l^2 - 4a^2)$$

$$s = 12E dy / (3l^2 - 4a^2) = 3aW/bd^2$$

where s is the maximum stress, E is the Young's modulus, d is the plate thickness, b is the plate width, l is the span, y is the deflection rate, w is the load, and a is the distance from the outermost fulcrum to the next fulcrum.

3) Slow Strain Rate Testing (SSRT)

Under a controlled environment, a specified tensile strain rate is given to the material, and cracking susceptibility and crack propagation behavior are evaluated from the obtained stress-strain curve, fracture ratio, and section shrinkage ratio.

Figure 3.1.20 shows an example of a testing apparatus. Combining tensile type specimens with a motor or gear, tensile stress is given and change in strain is measured by load cells and the stress-strain curve is obtained. This is performed in a noncorrosive atmosphere (nitrogen, argon gas, or oil) and the test atmosphere, and the maximum stress and strain values are compared or the reduction area ratio and fracture ratio in the test atmosphere are obtained for evaluation.

This test method has the problems that information related to the crack generating process is difficult to obtain and that a special testing apparatus with a strain rate control capability is required, but it excels in the capability to quantitatively evaluate susceptibility to stress corrosion cracking among materials for a short time.

(5) Corrosion Test under Heat Transfer²⁷⁻³⁷

Of the corrosion cases evolving in heat exchangers, a typical component which has a heat transfer surface in chemical plants, more than 70% of corrosion occur in heat exchanger tubes. That is, heat exchanger tubes handle two fluids of completely different properties, and moreover, the change of state takes place on the heat transfer surface due to evaporation and condensation.

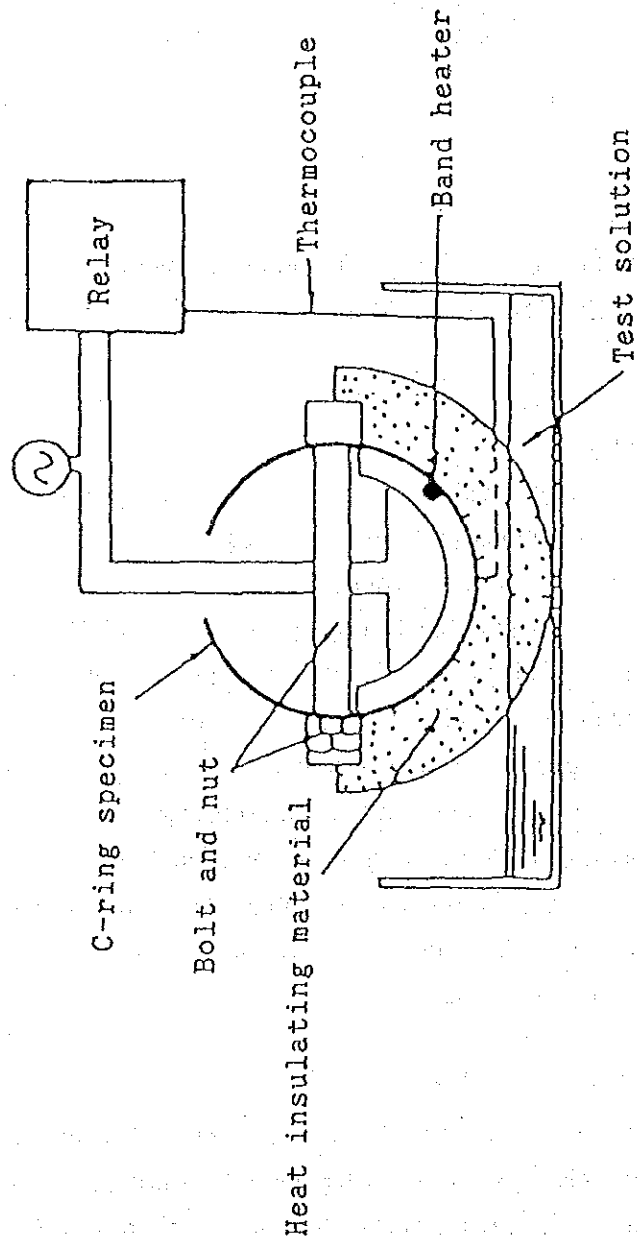


Fig.3.1.18 Wicking test method using C-ring type constant strain testing^s

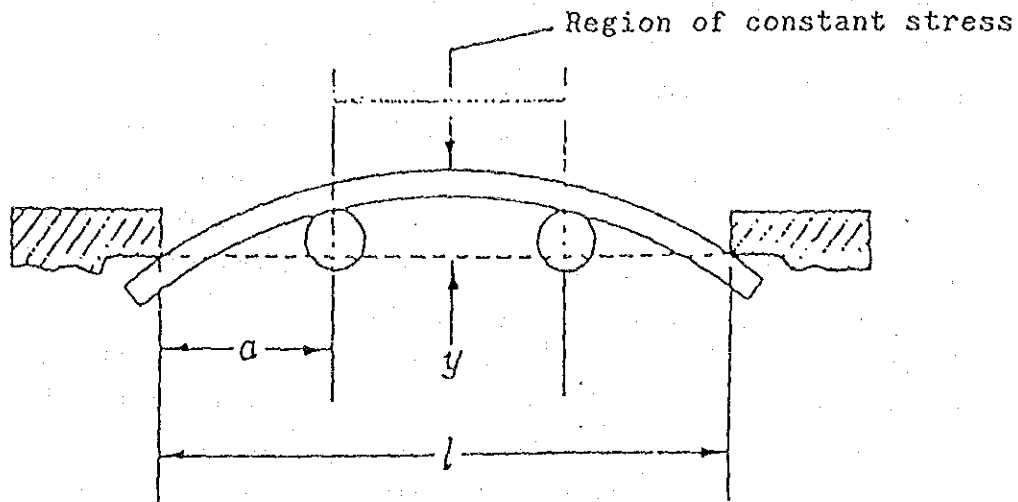


Fig.3.1.19 Stress application by 4-point support method¹

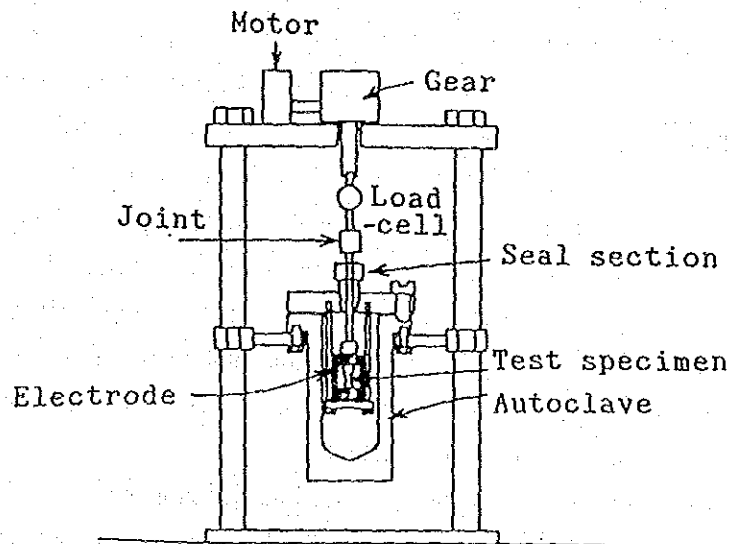


Fig.3.1.20 Testing apparatus by slow-strain rate testing²⁶

It is one of the severest environments from the viewpoint of corrosion. Various corrosion testing apparatus have been proposed to reproduce corrosion on the heat transfer surface. On the other hand, on the heat transfer surface, accumulation of corrosion products and precipitates from the fluids takes place in addition to boiling and condensation of the fluids. There are many tests on scaling, which has a direct effect on heat transfer efficiency. In general, corrosion on the heat transfer surface is subjected to surface temperature, heat flux, changes of state such as boiling and condensation, and scaling of the heat transfer surface, and such factors have been taken into account to design a heat transfer surface corrosion testing apparatus.

Figure 3.1.21 is a testing apparatus which investigates the effects of surface temperature and heat flux on the heat transfer surface corrosion of steel in an acidic solution. Two liquids with different temperatures are brought into contact via a specimen and the temperature gradient of the specimen cross section is governed by the temperature difference between the liquids on both sides. Corrosion rate of the specimen is calculated from the iron ions which flow out into the solution. The main feature of this apparatus is the capability of investigating the activation process of corrosion reactions on the heat transfer surface by varying the solution temperature. Similar testing apparatus have been reported.

Even in the same heat transfer surface corrosion, on the boiling heat transfer surface, boiling bubbles are said to have effects on corrosion. The heat transfer surface corrosion testing apparatus under boiling falls into two broad categories according to the type of heat source. Figure 3.1.22 is a heat transfer surface corrosion testing apparatus which uses steam as a heat source with an actual plant taken in to account. It can vary heat flux by adjusting steam pressure and amount. The specimen is tubular and the corrosion behavior at the boiling gas-liquid interface, which repeats drying and wetting, can be investigated by forming a gas-liquid interface on the specimen. The corrosion rate is found by directly measuring the change in tube weight. Figure 3.1.23 is an apparatus using a soldering iron or direct energization as a heat source. Compared to Figure 3.1.22, operation is easy and the apparatus is popularly used as a corrosion device for the boiling heat transfer surface, but since the metal surface temperature on the heat source side is higher than that in the case of steam, severer corrosive conditions are generated to simulate the heat transfer surface corrosion of actual plants.

In addition, also at the steam condensation section, which is the reversal of boiling, corrosion is apt to be accelerated. Titanium exhibits excellent corrosion resistance in boiling nitric acid, but corrosion test results of the condensed heat transfer surface where tubular titanium specimens are installed between the boiling flask and the water-cooling condenser indicate that, in some cases, the corrosion rate at the condensing section of the nitric acid vapor becomes more than 5 times that of the boiling nitric acid solution.

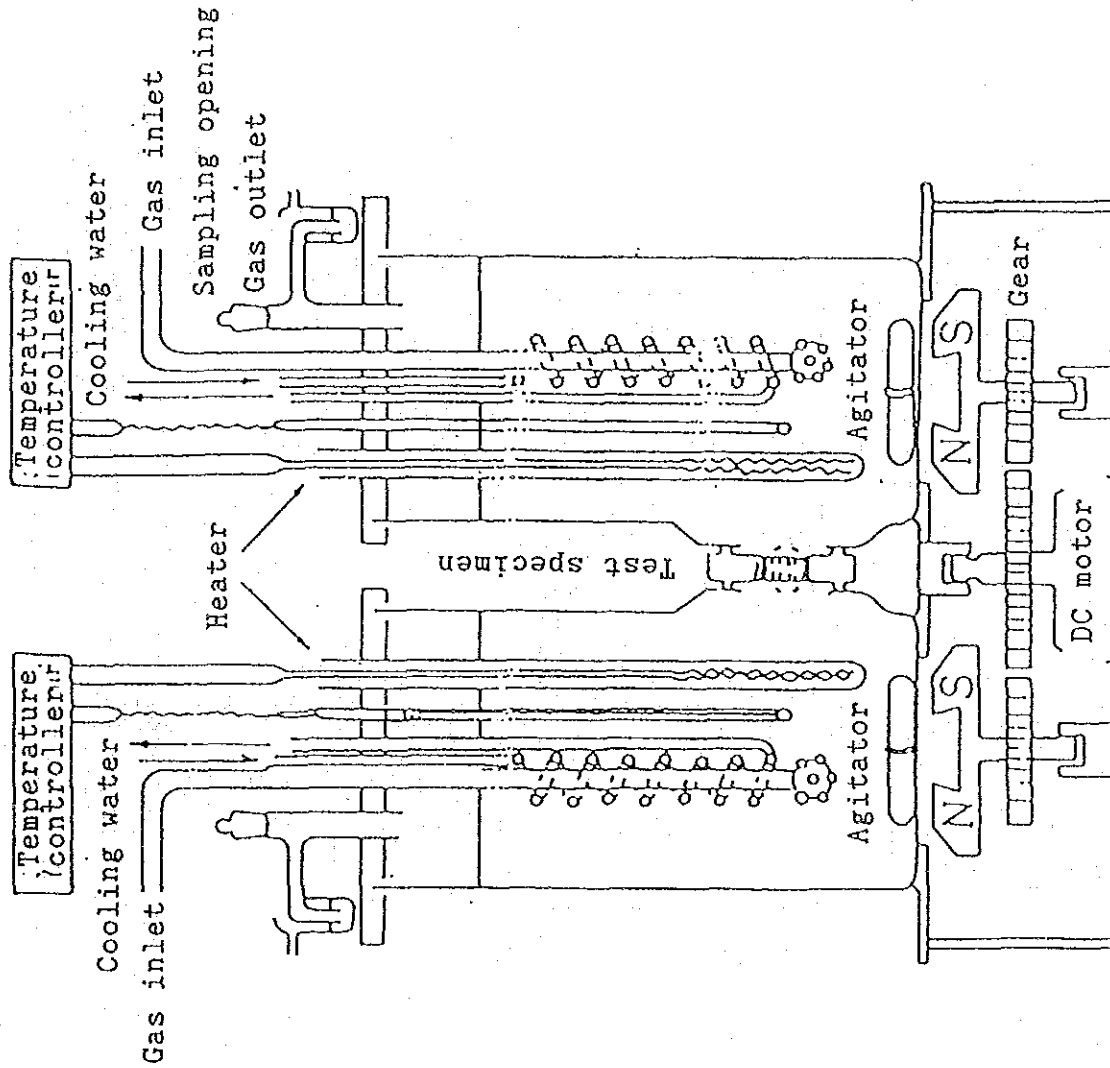


Fig.3.1.21 Schematic diagram of corrosion testing apparatus under heat transfer ⁵

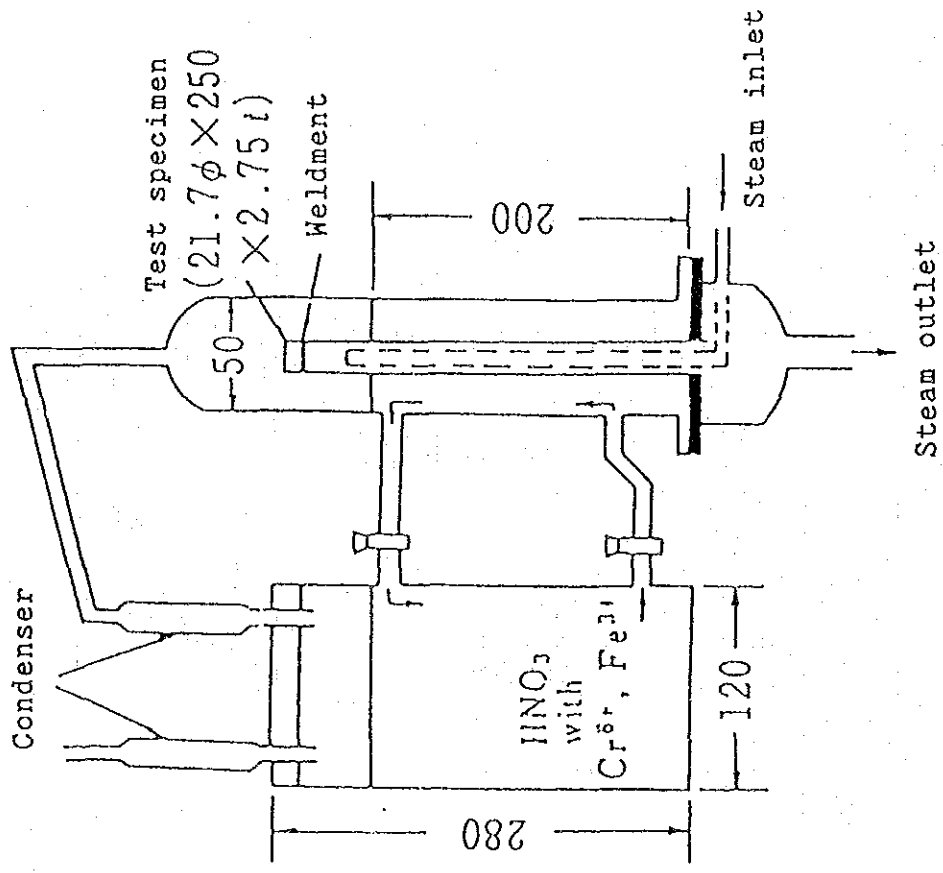


Fig.3.1.22 Boiling heating surface corrosion testing apparatus using steam heating⁵

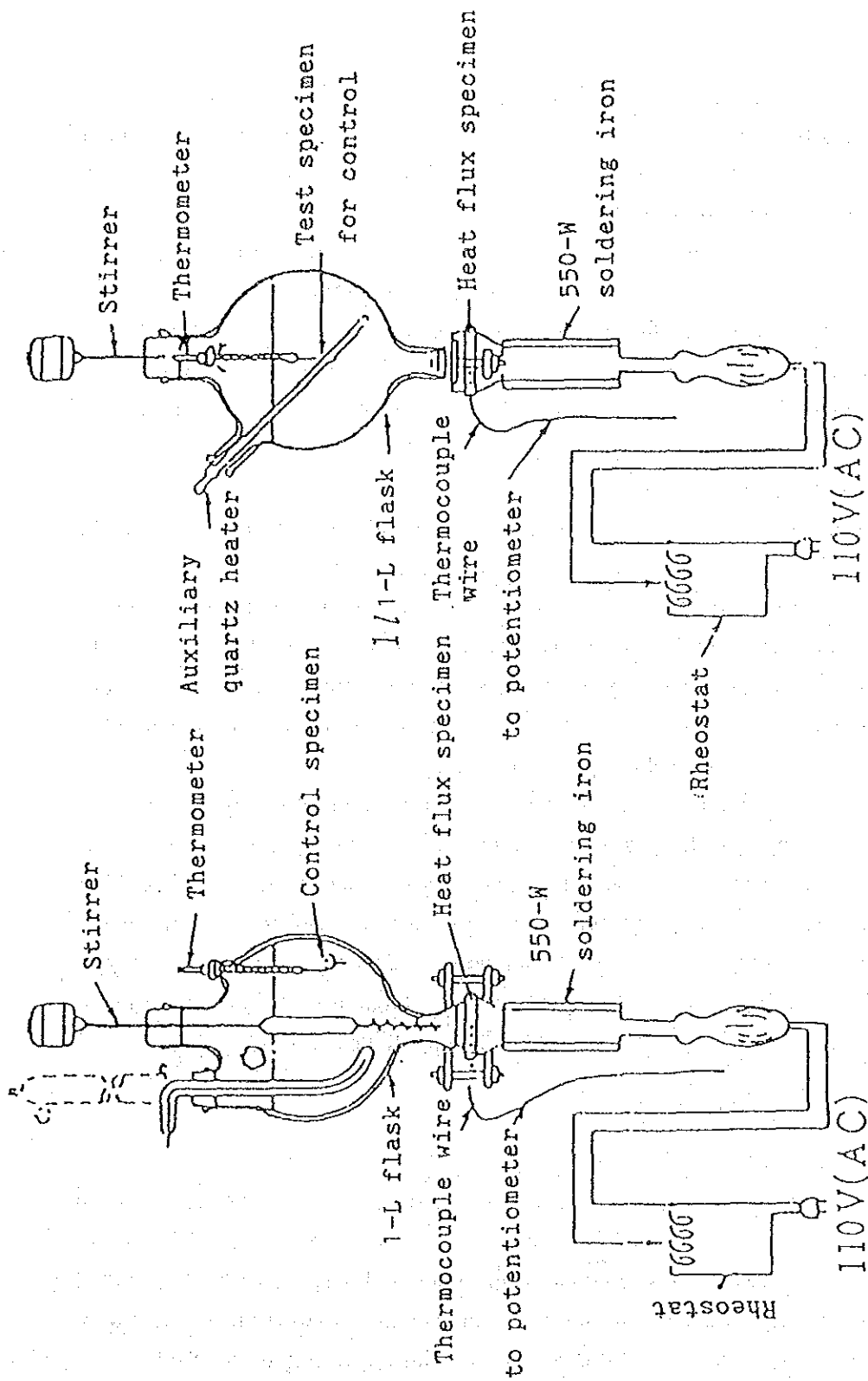


Fig.3.1.23 Heating surface corrosion testing apparatus at boiling point or lower^s
 (Left: cross section, right: 90° deviated cross section)

Figure 3.1.24 shows a testing apparatus which can carry out heating and cooling on the heat transfer surface with the liquid behavior taken into account to determine the corrosion behavior of the heat transfer surface. The testing section is formed into a double pipe; through the inside and outside pipes corrosive liquids of different temperatures are allowed to flow at specified flow rates so that heat flux and thermal stress can be investigated. Measurement of surface temperature, the most important factor when heat transfer surface corrosion is investigated, is carried out by directly inserting thermocouples into the pipe wall as shown in Figures 3.1.21 and 3.1.24, but recently new measuring methods have been proposed, such as direct measurement of heat transfer surface temperature using the p-n junction of semiconductors.

3.1.2 Corrosion Monitoring Testing Apparatus

In the corrosion phenomenon, the corrosion rates change with time, sudden propagation of localized corrosion can occur frequently after a certain incubation period, and subtle differences in environmental conditions may sometimes cause corrosion rates for actual equipment to differ from the values predicted from the laboratory level data. Consequently, it is extremely important to monitor the conditions of currently occurring corrosion in order to accurately understand corrosion phenomena and corrosion life, and this is a technique which has attracted the keen attention of industries and engineers throughout the world.

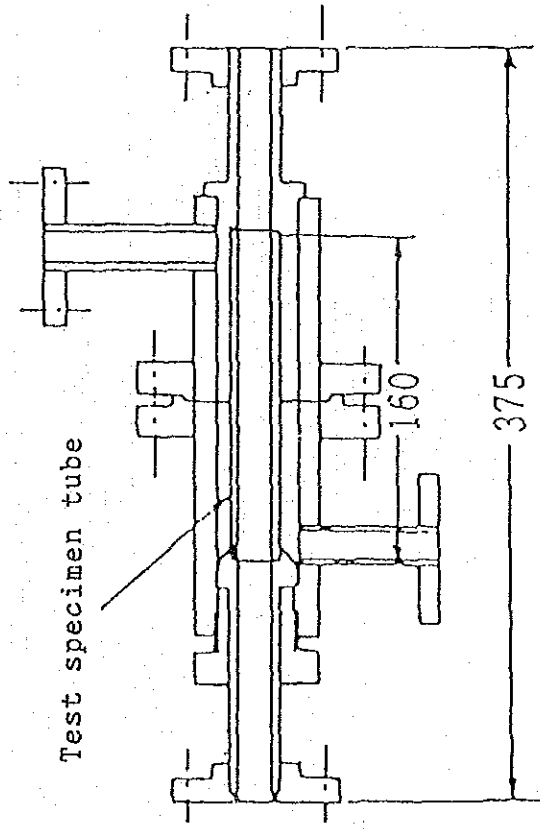
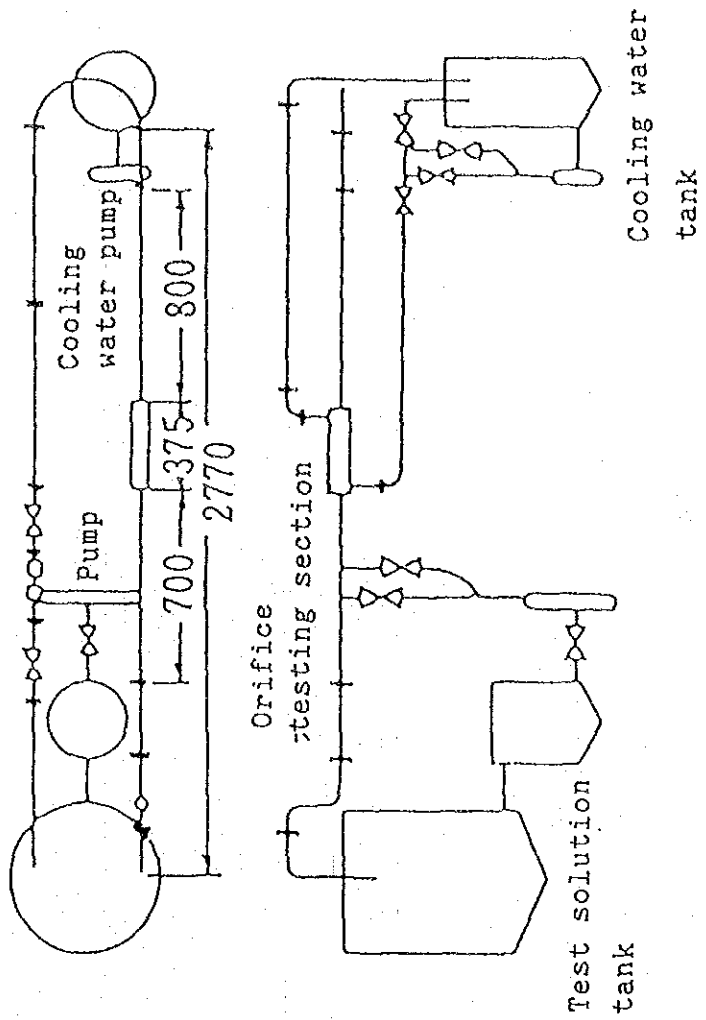
Therefore, in this investigation the corrosion monitoring technique is roughly classified into physical measuring methods (electric resistance probe, mass reduction measuring, thickness measuring, chemical analysis, and direct monitoring methods) and electrochemical measuring methods (electrode potential measuring, polarization curve measuring, and polarization resistance methods), and each measuring principle, the advantages, disadvantages, and precautions in measurement are summarized for the current technical level. Features of these various corrosion monitoring techniques are summarized as shown in the following Table 3.1.7.

(1) Physical Measuring Method ³⁷⁻⁴²

a) Electric Resistance Probe Method

Because electric resistance of metal is inversely proportional to the cross section when the length is constant, a decrease in wall thickness due to corrosion can be evaluated by an increase in electric resistance. Based on this principle, a specimen with a special form is installed to the apparatus and the change in corrosion rate with time is determined from the change in electric resistance of the specimen resulting from corrosion. This has a long established history as a corrosion measuring technique in actual plants and is extensively used primarily in the petroleum industry.

Since this does not operate on the electrochemical principle, application is not limited to



Testing apparatus

Testing section

Fig.3.1.24 Heating surface corrosion test under flow condition⁵

Table 3.1.7 Features of various corrosion monitoring techniques³⁷

Method	Description	Applicability	Limitation
Visual observation	Determination of corrosion modes and levels	Simple	1) Subjective 2) Qualitative
Microscopic observation	1) Identification of corrosion modes 2) Measurement of corrosion depth 3) Change in microstructure and composition	Auxiliary means	Semi-qualitative
Change in weight	1) Degree of general corrosion 2) Overall change	1) Simple 2) Quantitative 3) Direct	1) Total corrosion rates only 2) Error by corrosion products 3) Not applicable to localized corrosion
Change in thickness	Measurement by ultrasonic, X-ray, and eddy current	Quantitative	1) Total corrosion rates 2) Information on measured portion
Analysis of metallic ion in solution	Quantitative evaluation of corrosion rates	1) Measurable in traces 2) Instantaneous corrosion speed	1) Imperfect dissolution of products 2) Precipitates (sulfides, hydroxides)
Hydrogen generation rate	ditto	Instantaneous corrosion rate	Corrosion in acid only
Oxygen consumption	ditto	ditto	Oxygen consuming type corrosion
Electric resistance method	1) Quantitative evaluation of corrosion rates 2) Evaluation of environmental corrosiveness	1) Nondestructive 2) Continuous measurement possible	Indirect verification is required
Electrochemical method 1) Linear polarization method 2) Polarization measurement 3) Surface film resistance	ditto	1) Instantaneous corrosion speed 2) Continuous measurement possible	Interference by high resistance of film and solution
Change of mechanical properties	Identification of film insulation 1) Measurement of tensile strength, elongation, hardness, and cracking time 2) Stress corrosion, hydrogen embrittlement test	Evaluation of film protective properties Measurement of change in material properties	Total value only
In-situ investigation and statistical analysis	Collection and arrangement of corrosion accidents and investigation results	Total only	Time-consuming and costly

the electrolyte solution system but can be applied extensively to any environment including gaseous phase and soil. However, since the reading of electric resistance corresponds to the integrated value of the reduction of wall thickness caused by corrosion, it is necessary to calculate the time change of this value to determine the corrosion rate, which forms its sensitivity limit by itself. This is useful for tracking corrosion behavior over a long period, but is too slow to apply to real-time monitoring. Consequently, this apparatus could be used to compare the corrosion resistance of various materials in the system, detect the location (environment) suffering a large amount of corrosion, or check the change in the corrosion rate with the lapse of about ten hours in the reaction system.

With this method, penetration depth can be accurately determined when specimen wall thickness decreases uniformly by general corrosion or erosion, but problems arise in the case of nonuniform corrosion. However, since formation of localized corrosion governs all the resistance even if only partially corroded, it is possible to detect formation of localized corrosion such as pitting from abnormal increases in resistance.

Figure 3.1.25 shows a general view of the apparatus. It is marketed under the brand name "CORROSOMETER" (manufactured by Magna Company), and is available in two types: manual portable type and stationary type, both of which enable automatic measurement. The measurement and detection capability is about $0.2 \mu\text{m}$. The test specimen is embedded in a probe in the form of the letter U and the portion exposed to the corrosive environment is designated as a corrosion specimen. The ratio of resistance to the reference specimen at the seal section is measured with the bridge of a gauge. The reference specimen has the role of providing temperature compensation as well as providing a specified resistance. As consumption of the corrosion specimen progresses, the new equilibrium point is found to determine penetration depth. The check specimen detects a change in resistance of the reference specimen due to damage to the seal.

Three types of specimens are available; ribbon, tube, and wire. Probes are available in various types of construction to be suited for each application, such as fixed type which is installed by screw-in or flange, removable type which enables replacement of specimens without stopping apparatus operation, or flush mount type which has no protrusion in the liquid and can measure resistance without disturbing the liquid flow.

Information obtained from this probe is used to confirm the general corrosiveness of the test environment, but because the inside of actual equipment is nonhomogeneous and contains other various uncertain factors, controlling the corrosion of the equipment only based on the information from the probe may result in an unexpected corrosion failure. Examples include the adhesion of precipitates in the liquid to the probe tip end (particularly frequent under high temperatures), in which a value of 0.01 mm/yr or less is furnished as information but the equipment

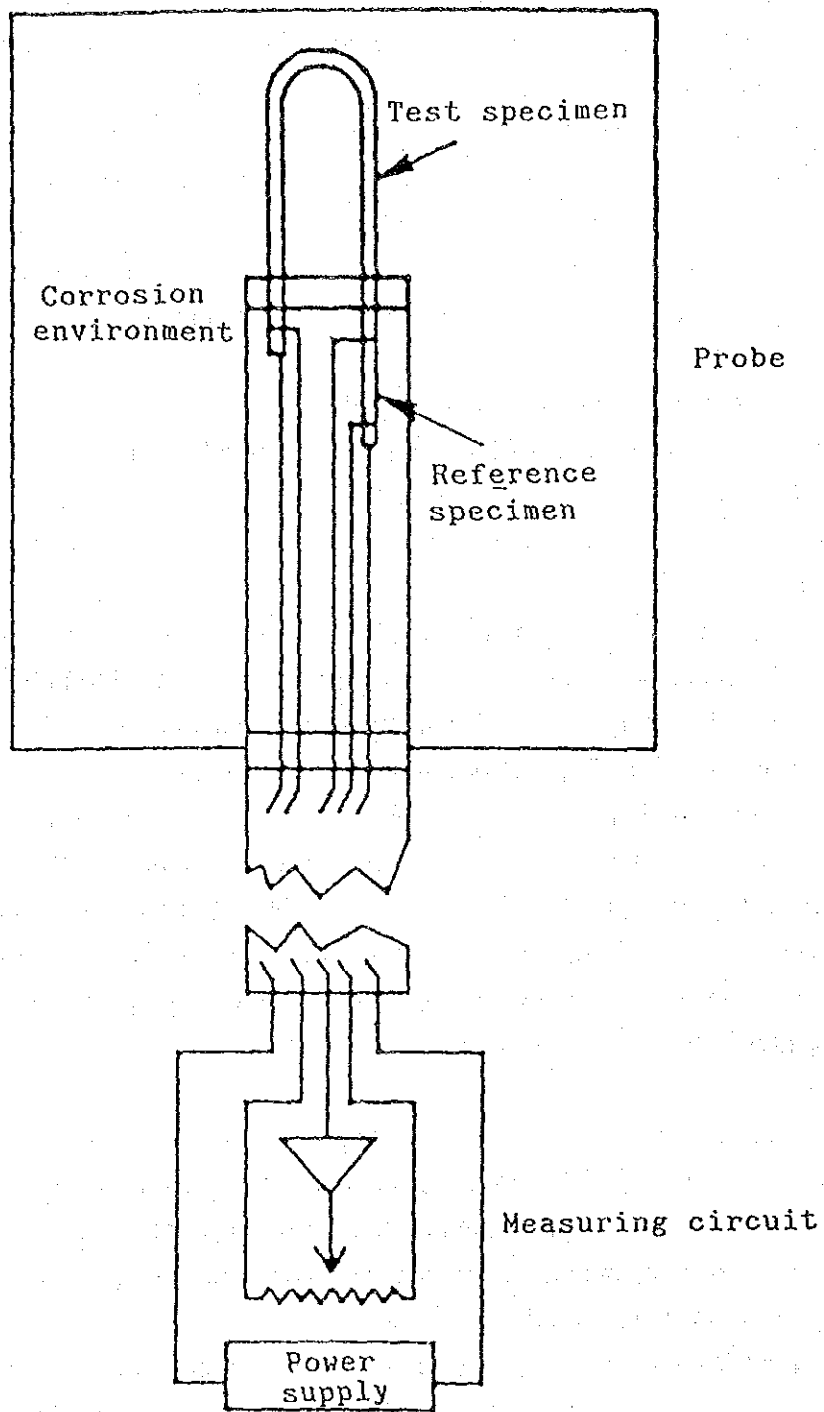


Fig.3.1.25 Measuring gauge by electric resistance method³⁸

causes leakage due to corrosion in about one year. This is the case whether the probe comes in constant contact with the new liquid or not, and failure to provide a means to check this condition would constitute a problem. Consequently, it is desirable to use this method in combination with metallic ion analysis (Fe, Ni, Cr, Ti, etc.) in the system.

b) Mass Reduction Measuring Method

The mass reduction measuring method is the most basic and important method by which specimens are installed in the actual equipment, periodically taken out to measure reduction in mass and by which the corrosion rate is examined. Because this method calculates a mean corrosion rate from an integrated value of corrosion during a specified period and in the overall surface of the specimen, it has the disadvantage that it is not possible to determine the instantaneous value when the corrosion rate varies with time or when corrosion is localized, as the indication as a mean value does not have any significance. However, the use of a creviced specimen or a self-loading type stress corrosion cracking specimen makes it possible to judge whether crevice corrosion or stress corrosion cracking is generated or not.

The profile, size, and surface condition of specimens are determined depending on the test purposes. The conditions required for specimens include the following:

- 1) The ratio of the surface area to weight must be maximized to minimize error (avoid reducing thickness to cause penetration).
- 2) Because the cross section of a plate or forging has poorer corrosion resistance than the worked surface, its ratio must be minimized.
- 3) Excessively small total surface area makes it difficult to generate localized corrosion. Provide as large a total surface area as possible.

Prior to testing, polishing, degreasing and rinsing, drying, and weighing (to 0.1 mg) shall be carried out, and at least two specimens shall be prepared in view of variations in data.

Specimens must be held in such a manner as to stand long-term tests even under severe environmental conditions. In general, to avoid detachment of specimens or contact of one specimen with another or specimens with the equipment wall, specimens are assembled in a rigid spool holder built with bolts and nuts and fixed into the equipment. Figure 3.1.26 shows examples of spool holders and specimens. In a confined place or pipe where a large-size spool holder cannot be placed, a holder and a specimen as shown in Figure 3.1.27 are recommended for use. Metal which exhibits sufficient corrosion resistance under the test environment must be selected as the holder material. Teflon is popularly used as an insulation material because of its excellent corrosion resistance under any environment.

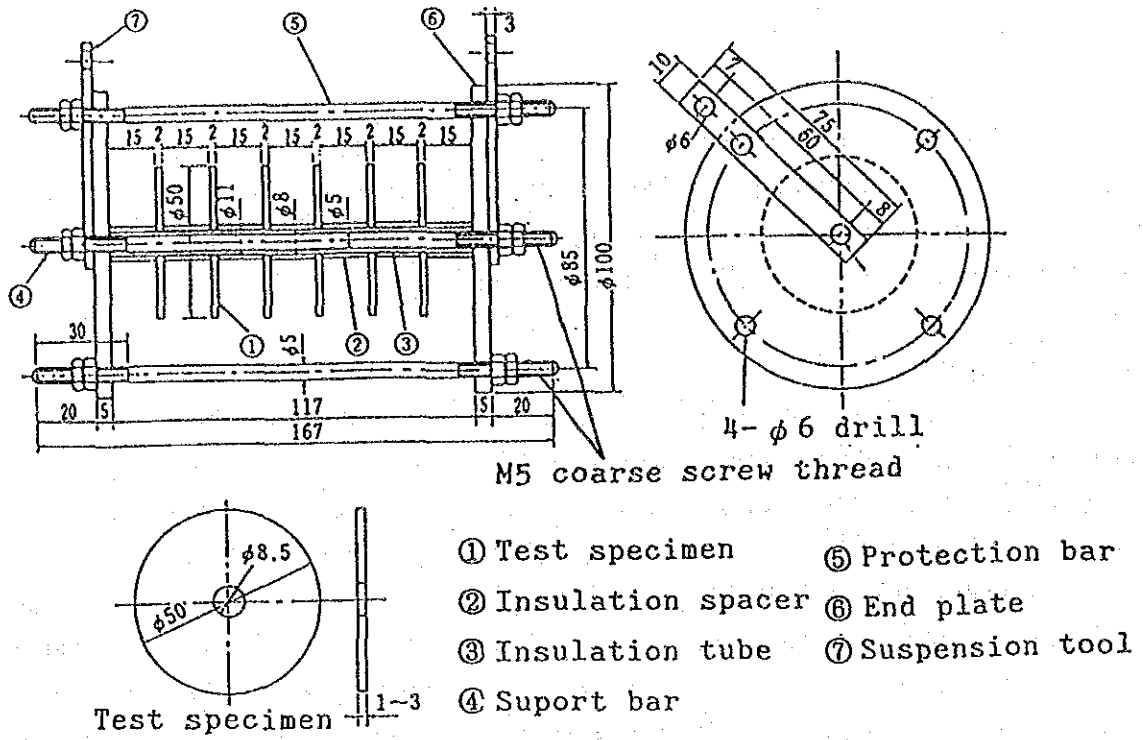


Fig.3.1.26 Example of spool holder and specimen ⁵

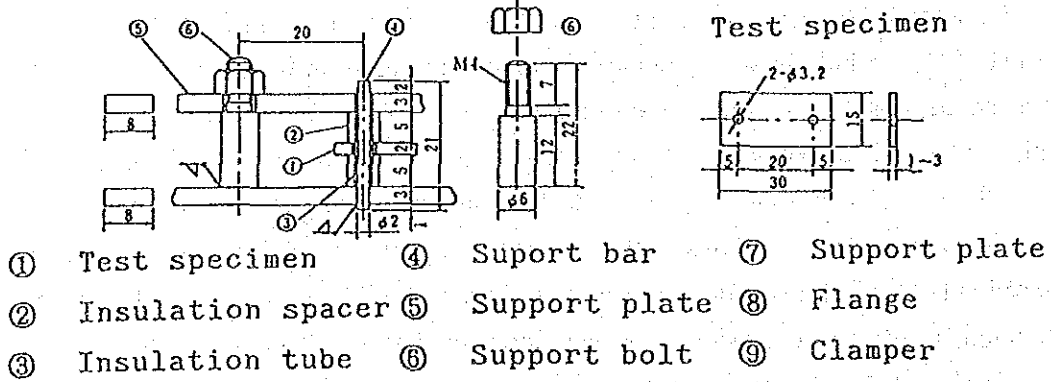
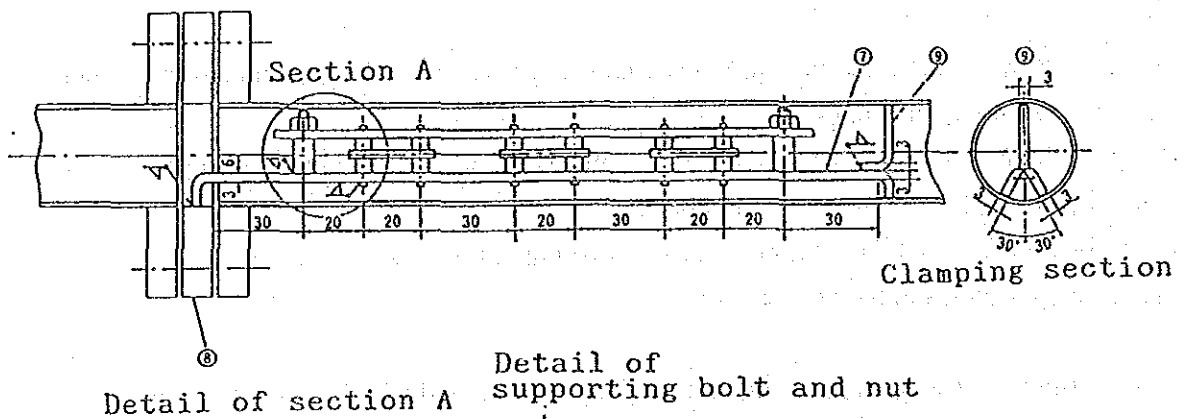


Fig.3.1.27 Example of pipe holding jig and specimen ⁵

With respect to test time, it is desirable to take a longer time when the corrosion rate is small, from the viewpoint of accuracy. As a rule-of-thumb, test time (h) = 50/corrosion rate (mm/yr) is generally used. To remove corrosion products from specimens after tests, a mechanical method using a brush or ultrasonic wave, a chemical method using a solvent or inhibitor-added acid, or an electrochemical technique using cathodic polarization are used depending on the conditions. If corrosion is excessively nonuniform, the depth of the maximum eroded portion should be measured.

c) Thickness Measuring Method

An ultrasonic pulse reflection measuring method is frequently employed to measure thickness at a fixed point. When visual inspection of the inner surface such as piping is impossible and total plane inspection is required, radiographic examination and eddy-current flaw examination are employed.

1) Ultrasonic Thickness Gauge

The pulse type ultrasonic thickness gauge transmits ultrasonic pulses from a contact, detects pulses reflected from the pulse rear surface, and determines the thickness from the time required for pulses to reach the opposite surface and return. Inputting the sound velocity of the measured material enables the digital display of measured values.

Irregularity on the rear surface is often excessive and measurement cannot be performed, or a large variation is frequently shown, sometimes constituting problems between inspectors and clients. Consequently, in measuring, it is necessary to state the inspected portion, measuring device, measuring personnel, number of measurements per place, and recorded values (minimum, mean, and typical values). In addition to this, when thickness of the measuring section approaches the lower limit value, thickness two to three times greater than the actual thickness is sometimes displayed though measurement is actually rejected. Accepting the complete value results in an unreliable judgment, to which caution must be shown.

In the case where corrosion rate is high enough and corrosion over a period of only one year has developed to the extent that can be detected by this method, the equipment may cause leakage frequently due to localized corrosion at welds or other places before the detection. Furthermore, this measuring method is point measurement from the outside and therefore, it is nearly impossible to determine the remaining wall thickness at the most severely corroded portion. Consequently, this is not sufficient as a corrosion prevention control method to check the degree of corrosion or to prevent leakage due to corrosion.

2) Radiographic examination

When there is a danger of leakage due to localized corrosion or erosion near the weld, overall inspection is difficult to perform using an ultrasonic wave thickness gauge and therefore radiographic examination is carried out.

Figure 3.1.28 shows an example of X-ray photography of a small-diameter pipe. In this case, since the section 1 is a profile of the pipe wall, it is possible to read the remaining thickness directly from the photo. On the other hand, the dent at section B exhibits a darker color than at other places. Therefore, the thickness of section A is measured with an ultrasonic thickness gauge while the densities at A and B are measured with a densitometer (density of the 1-mm-diameter portion is measurable). Then, using Figure 3.1.29, which shows the density-plate thickness relationship determined previously by varying voltage and exposure time of the X-ray equipment, a known point A is plotted on the figure and the remaining thickness is estimated from the density at point B on the curve. The measurement accuracy by this method is about 5% of the wall thickness.

In this way, the radiographic control is a plane inspection, which is an indispensable method for control of localized corrosion inside pipes and those portions with a double structure. The combined use of an ultrasonic thickness gauge will further improve control performance.

3) Eddy-current Flaw Examination

This is a technique to detect the eddy current generated in metal placed in the magnetic field of a coil and to determine metal thickness. Figure 3.1.30 shows an example of a commercially available displacement gauge. It is popularly applied to inspection of localized corrosion and cracks of non-magnetic tubes such as copper, copper alloys, stainless steel, and titanium. It is a technique designed to insert a high-frequency current energized sensor into a tube, move at a specified speed, and detect the change in an eddy current induced in the tube in the vicinity of flaws as a change in impedance of the coil in the sensor.

The eddy-current flaw detector is able to perform 100% inspection in a comparatively short time (700-1000 pcs. per day), yet there are many factors that prove influential during inspection. Therefore, a high level of skill is required when excellent quantitative accuracy and reproducibility are required.

d) Chemical Analysis

Chemical analysis methods include pH measurement, metal and various ion analysis, measurement of the amount of evolved hydrogen and consumption of oxygen, and ICP analysis.

pH measurement is important for identifying the corrosiveness of the environmental on the metal, and in particular, it can be determined whether the corrosion conditions of passive metal are in the active or passive state by electrode potential and pH.

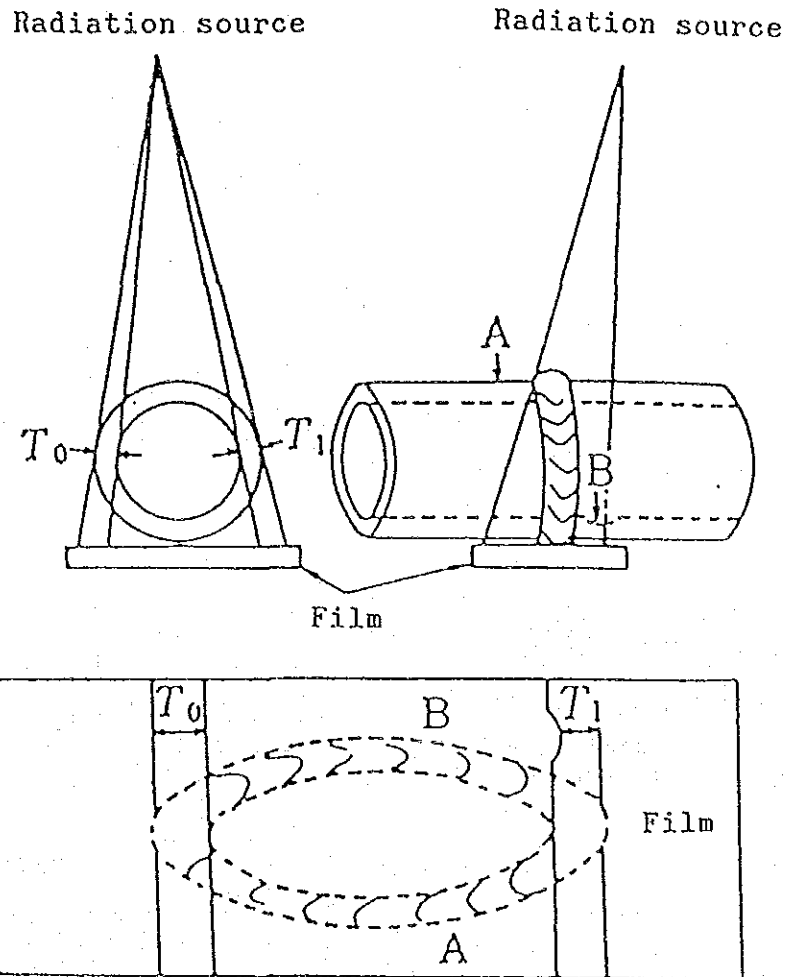
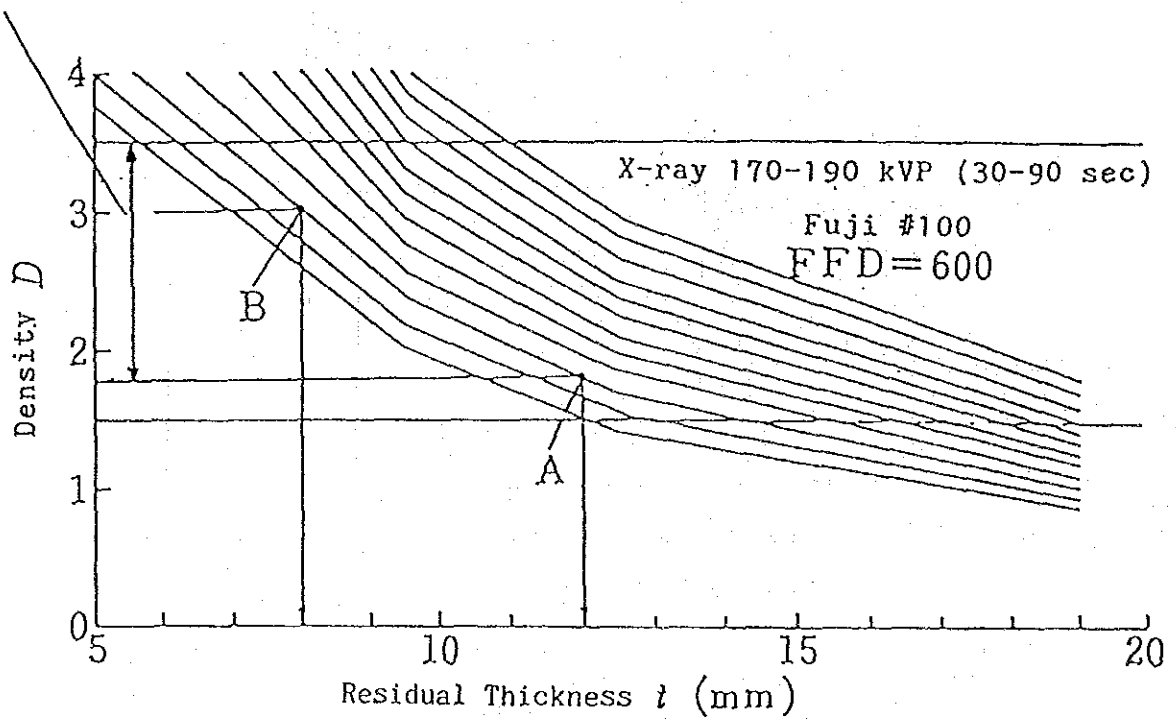


Fig.3.1.28 Measurement of pipe thickness by radiographic examination ⁵

Effective identification range



Point A is known thickness.

Thickness at Point B is estimated from density.

Fig.3.1.29 Basic diagram to find residual thickness from density of X-ray radiographic film ⁵

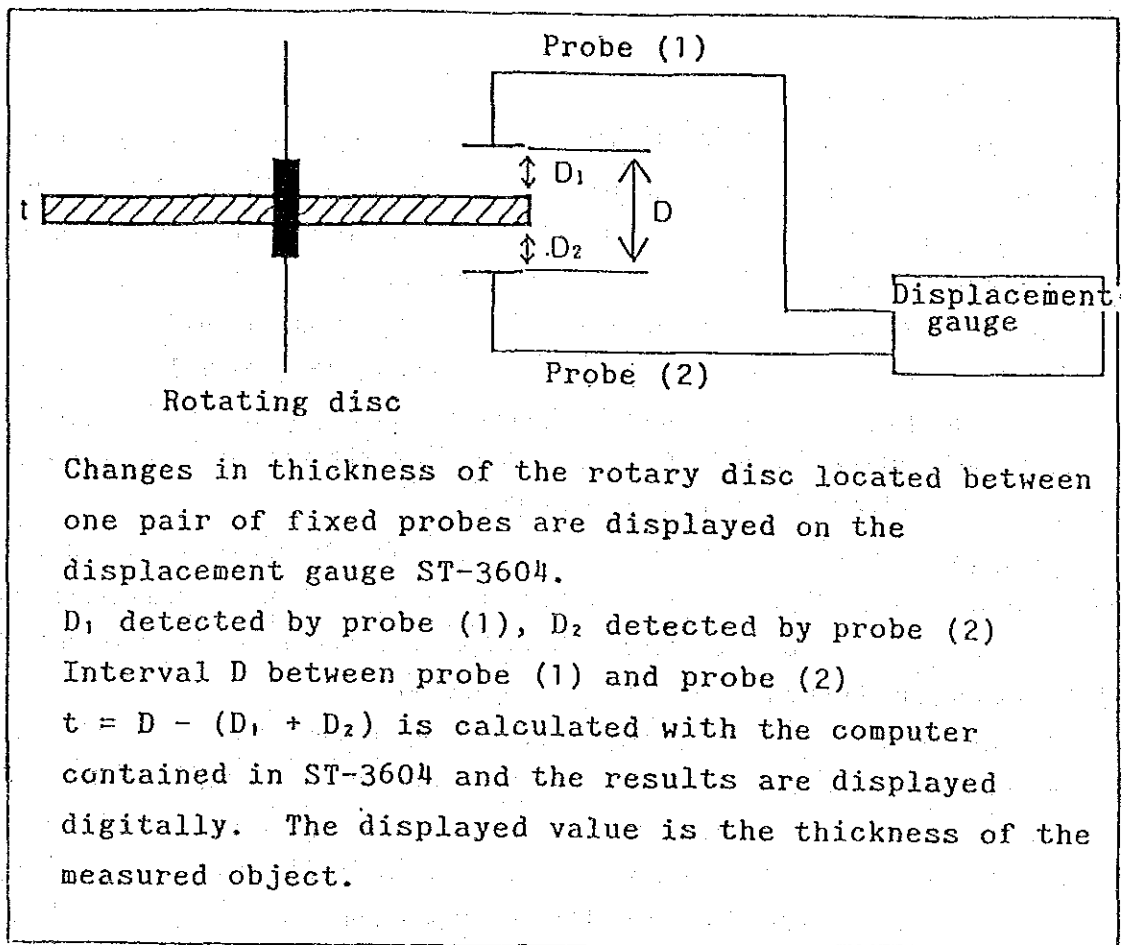


Fig.3.1.30 Measurement of metal sheet thickness ⁴¹

Analysis of metallic ions in a liquid has a feature to enable quantitative evaluation of corrosion, and even traces of metallic ions and an instantaneous corrosion rate can be measured. However, it has limitations due to the imperfect dissolution of products and deposition of sulfides and hydroxides.

Measurement of hydrogen evolution rate and oxygen consumption enables measurement of the instantaneous corrosion rate and contributes to the quantitative evaluation of the corrosion rate, but the use of the former is limited to corrosion in the acid and the latter to oxygen consuming corrosion.

1) Measurement by Ion Sensor

The ion sensor represented by the pH sensor is called an ion (selective) electrode and responds to a specification. The principal part is an ion selective membrane and the membrane potential varies depending on the concentration of the ion subjected to measurement. That is, the ion concentration is measured by the membrane potential of the ion selective membrane.

Figures 3.1.31 and 3.1.32 show the typical configuration of an ion sensor. In general, the ion sensor consists of a reference electrode, an inner standard solution, and an ion selective membrane. There is a case in which the metal of an ion selective membrane is directly connected or no internal standard solution is contained. For a reference electrode, saturated calomel electrode (SCE), or silver/silver chloride electrode is used.

The potential difference between the reference electrode inside the ion sensor and the external reference electrode corresponds to the membrane potential. There is a type which incorporates an external reference electrode to form an integral sensor. There is also a type which incorporates a thermistor for temperature compensation.

The internal resistance of glass-membrane or liquid-membrane type ion sensors is thousands of ohm to hundreds of thousands of ohm. Some of the slightly soluble salt solid membrane type sensors are available with an internal resistance of 1000 ohm or lower, but if there is an electrometer (potentiometer) of input impedance over 10^{12} ohm, it can be applied to all ion sensors. An electrometer that can read to 0.1 mV is desirable.

The measuring solution is agitated with a magnetic stirrer. Care must be taken to prevent generation of air bubbles. It might be necessary to place a plastic plate between the stirrer and measuring vessel for thermal insulation or to keep the measuring vessel temperature constant.

Table 3.1.8 shows major commercially available ion sensors according to ions to be measured. The calibration curve method, standard addition method, and potential difference titration method are methods to analyze the ion sensor output. The calibration curve method is designed to prepare calibration curves for ions to be measured and to determine the ion concentration by comparing the curves with ion sensor output. This is the easiest method of all. When

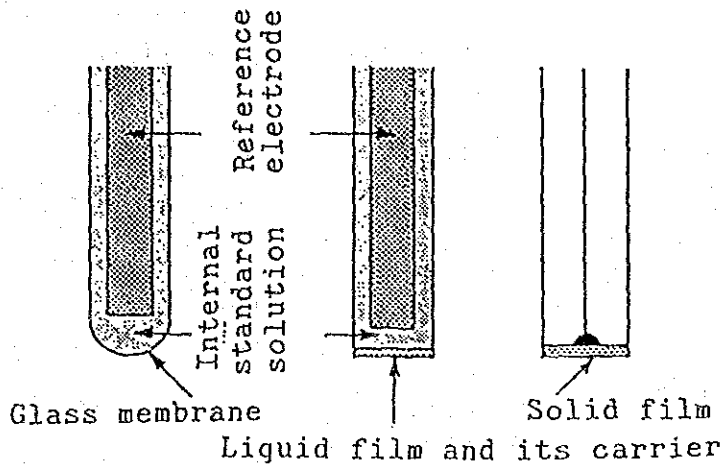


Fig.3.1.31 Construction of ion sensor ⁴³

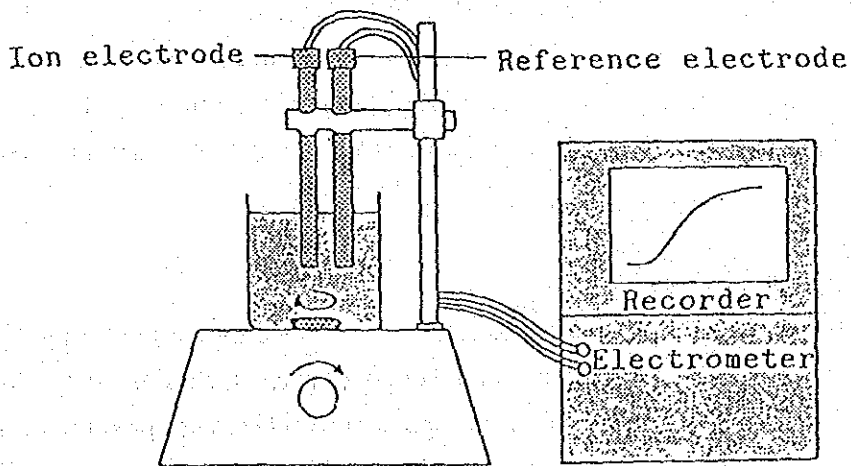


Fig.3.1.32 Measuring system of ion sensor ⁴³

Table 3.1.8 Major commercially available iron sensors⁴³

Measured ion	Measuring range	Major interfering component	Measured ion	Measuring range	Major interfering component
H ⁺	0 ~ 10 pH		CN ⁻	1 ~ 7 pCN	I ⁻
Na ⁺	0 ~ 5 pNa	H ⁺ , NH ₄ ⁺ , Li ⁺ , K ⁺ , Rb ⁺	S ²⁻	1 ~ 6 pS	Ag ⁺ unable to coexist
K ⁺	0 ~ 6 pK	Rb ⁺ , Cs ⁺ , NH ₄ ⁺	F ⁻	1 ~ 6 pF	OH ⁻
Li ⁺	0 ~ 5 pLi	H ⁺ , NH ₄ ⁺ , Na ⁺	NO ₃ ⁻	0 ~ 5 pNO ₃	I ⁻ , SCN ⁻ , MnO ₄ ⁻
NH ₄ ⁺	0 ~ 6 pNH ₄	K ⁺ , Rb ⁺ , H ⁺	Ca ²⁺	0 ~ 6 pCa	Zn ²⁺ , Fe ²⁺
Ag ⁺	0 ~ 7 pAg	S ²⁻ unable to coexist	Ba ²⁺	0 ~ 5 pBa	H ⁺ , K ⁺ , Rb ⁺ , Sr ²⁺
Br ⁻	0 ~ 6 pBr	CN ⁻ , I ⁻ , S ₂ O ₃ ²⁻	Cd ²⁺	0 ~ 6 pCd	Fe ²⁺ , TI ⁺ , Rb ⁺ , Mn ²⁺
Cl ⁻	1 ~ 5 pCl	CN ⁻ , I ⁻ , S ₂ O ₃ ²⁻ , Br ⁻			H ⁺ , Al ³⁺ , Ni ²⁺ , Co ²⁺
I ⁻	0 ~ 7 pI	CN ⁻	Cu ²⁺	0 ~ 6 pCu	Ag ⁺ , Hg ²⁺ , Fe ³⁺

The same as Fig.3.1.31

the ion strength is small and the activity coefficient can be regarded as 1, the ion concentration can be calculated from measured values. The standard addition method is to increase or decrease the measured components in the sample solution by a specified amount and determine the concentration from a change in sensor output. The potential difference titration method is designed to use the ion sensor as an indicator electrode for the titration end point and carry out potential difference titration.

2) Measurement of Evolved Hydrogen Amount

In the acidic solution, a metal corrosion rate can be determined by measuring the hydrogen amount generated by corrosion. To monitor corrosiveness of such an environment, a hydrogen probe (Figure 3.1.33) comprising thin-wall steel pipe is used. There are pressure type and vacuum type hydrogen probes. The former measures with a hydrogen gauge the pressure generated when the hydrogen atoms generated by corrosion of the probe diffuse into steel and recombine in the pipe to form hydrogen molecules, whereas the latter ionizes in vacuum the hydrogen atoms which have penetrated steel and measures the reaction current. Figure 3.1.34 shows one

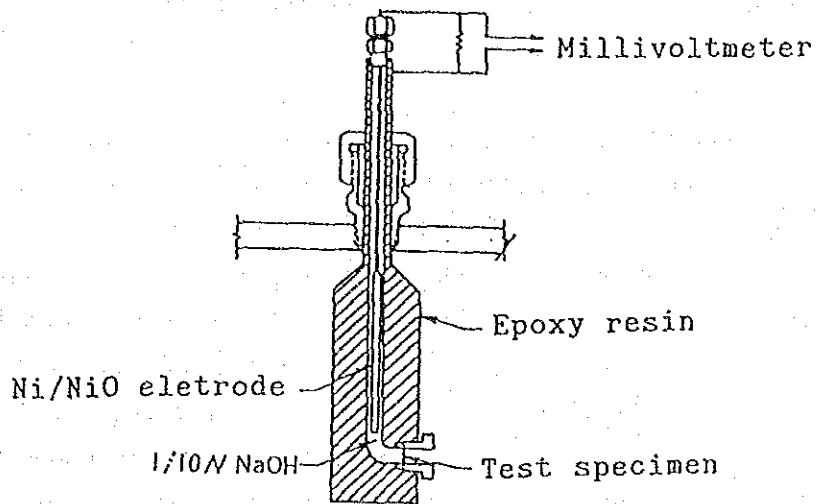


Fig.3.1.33 Hydrogen probe ³⁸

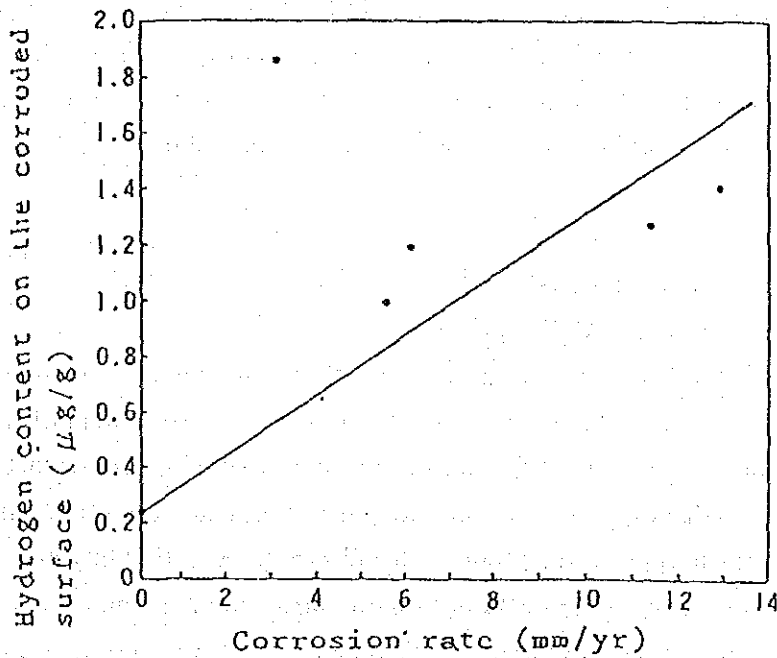


Fig.3.1.34 Relationship between hydrogen content on the corroded surface and corrosion rate determined by the supersonic thickness measuring equipment at an actual plant(carbon steel) ⁴⁴

example of the relationship between the hydrogen content on the corroded surface of carbon steel in actual plants and the corrosion rate determined by the ultrasonic thickness gauge.

3) ICP Analysis

This method measures the light emitted when atoms excited by inductively coupled plasma, ICP, discharge or outer electrons of ions transit to the lower energy level again. Qualitative analysis can be carried out from the wavelength position of the spectral line and quantitative analysis from intensity. The analysis can be applied to the solution samples, and it provides high sensitivity and achieves simultaneous determination of many elements ranging from low to high concentrations. The basic configuration of the general emission spectral analyzer is likely to be that shown in Figure 3.1.35, but the ICP emission spectral analyzer is equipped with a discharge tube (torch) and high-frequency power supply, argon gas, sample container, and atomizer, as shown in Figure 3.1.36, in place of a light emitting device and sample electrode, and light is measured optically.

e) Direct Observation Method

It is possible to directly monitor the pipeline with a fiber image scope using a bundle fiber or with a small camera. Figure 3.1.37 shows a super miniature industrial camera recently developed. It is reported to be 12 mm in diameter, 35 mm long, and 7 g in weight. It can be separated 10 meters away at maximum from the control section (Matsushita Communication Industrial Co., Ltd.).

(2) Electrochemical Measurement Method^{5,47-54}

a) Electrode Potential Measurement Method

Measurement of corrosion potential is fundamental to electrochemical measurement of corrosion and is carried out in almost all laboratories. Because measurement of the electrode potential does not require that energy be deprived from the measured object or that stimulation be provided, it is free from disturbing the system during measurement. Therefore, this is an ideal measuring method for monitoring. Information on the electrode potential only cannot generally serve as direct information, such as the quantification of corrosion rates, but constitutes significantly useful information as it is if polarization characteristics of the system are measured in advance. (There is the possibility of estimating the corrosion situation or corrosion rate.) In particular, this information is very useful for monitoring the corrosion mode which is extremely dependent on potential: i.e. whether the corrosion state of metal is active or passive, or whether localized corrosion is likely to occur or propagate. The Pourbaix Diagram identifies whether metal is in the active, passive or transpassive state, indicating the potential region of the

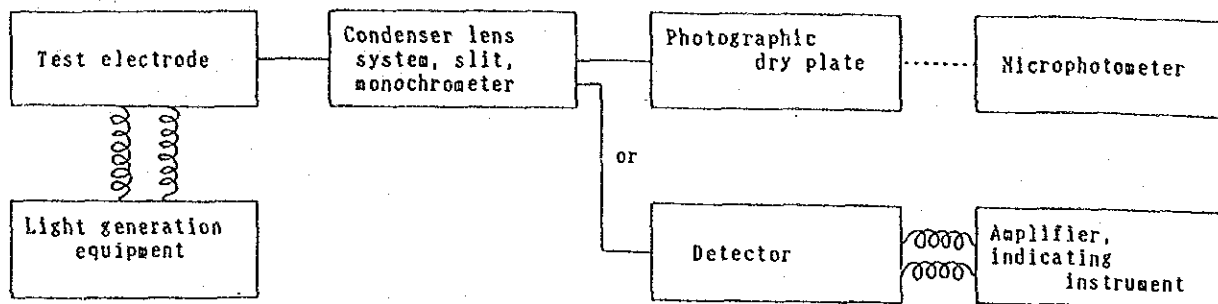


Fig.3.1.35 Basic configuration of emission spectrophotometer ⁴⁵

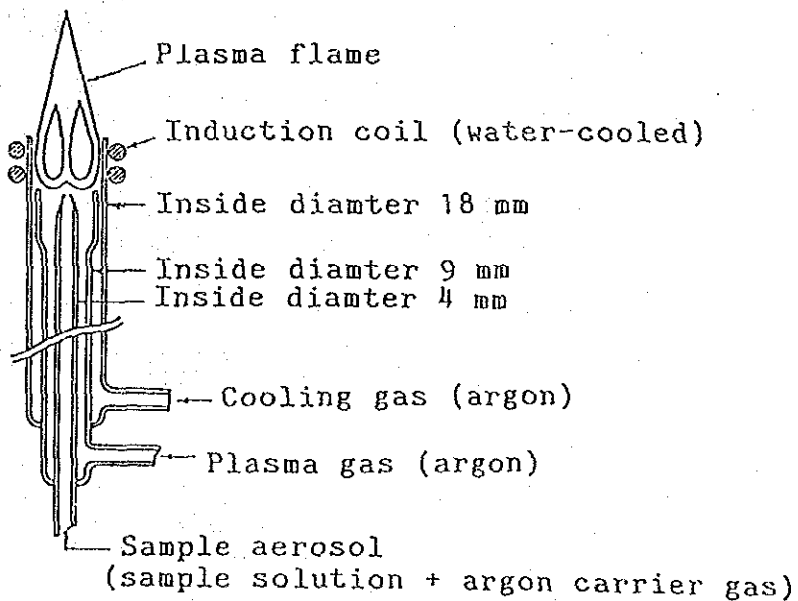


Fig.3.1.36 Inductively coupled plasma discharge tube ⁴⁵

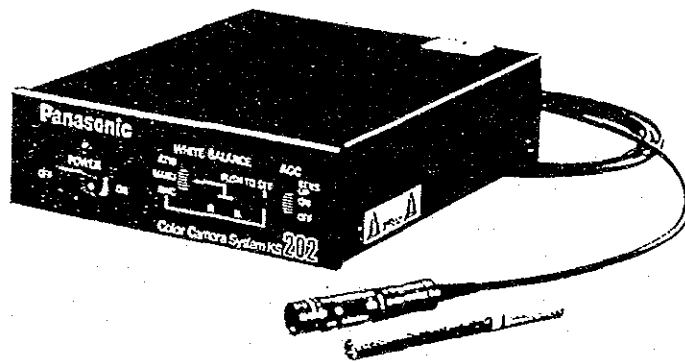


Fig.3.1.37 General view of supermicro camera ⁴⁶

condition that must be regulated with respect to a given environment. This suggests that the corrosion rate is not necessarily determined but that corrosion reactions can be controlled by regulating the potential.

As a corrosion test in-situ, corrosion potential measurement has advantages of the simplest equipment configuration, easy operation and maintenance, and continuous long-term nondestructive measurement.

Chloride localized corrosion such as pitting, crevice corrosion, and stress corrosion cracking of passive metal represented by stainless steel has the critical potential which determines the go-no-go boundary of corrosion in the course of its generation and propagation. The critical potential can be measured on the laboratory level using the process solution sampled at the site and comparing it with the corrosion potential in the actual equipment, which enables judgment during operation of whether corrosion will take place or not.

To measure the corrosion potential, designate the measured equipment as a sample electrode, measure the potential with the reference electrode installed in the sample electrode with a potentiometer, and record the results (Figure 3.1.38).

As reference electrodes, examples include a saturated calomel electrode, a silver-silver chloride electrode, and a copper-copper sulfate electrode. Among these candidate electrodes, a suitable one is selected considering major ion species, pH, temperature, and pressure of the environment. The double junction type electrode which has a double internal solution is convenient to achieve high accuracy. To install glass electrodes on the equipment wall, tapered rubber O-rings are used to prevent leakage and protect electrodes. Metal nets or perforated metal sheets may be used for protection covers depending on the internal conditions.

Under severer conditions, glass electrodes which contain liquid in themselves cannot be used and solid electrodes are required. For example, under the chloride environment, uncovered silver-silver chloride electrodes are used or corrosion electrodes composed of metal only are adopted. As an example of the latter, there is a pure zinc electrode which is popularly employed in a seawater environment. These electrodes are more subjected to fluctuations in environmental conditions than regular reference electrodes, and preliminary calibration and familiarization of the variation range during measurement are required, but intended results can be achieved even if the absolute value of the potential is unable to be measured accurately.

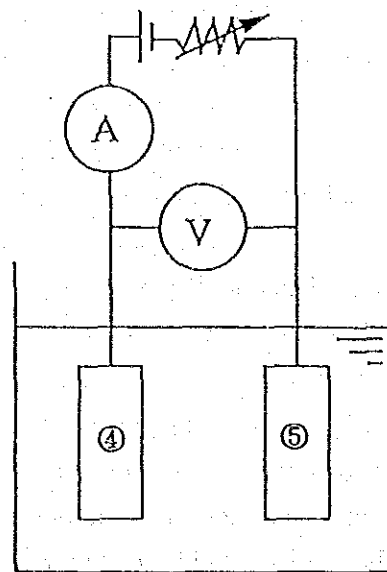
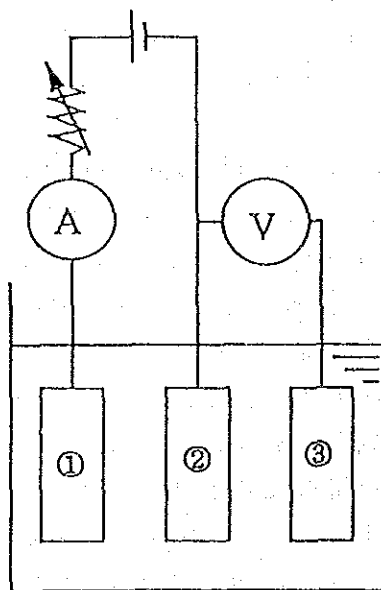
In-situ measurement of the potential under a high-pressure environment is even more difficult. In such a case, the reference electrode is placed either in the high-pressure system or in the normal pressure section outside.

b) Polarization Curve Measuring Method

Because corrosion of metal in the solution proceeds by electrochemical reactions, this method

(a) Three-electrode method

(b) Two-electrode method



- ① Counter electrode
- ② Test electrode
- ③ Reference electrode

- ④ Test electrode
- ⑤ Test electrode

Fig.3.1.38 Electrode system and measuring apparatus³⁹

has advantages in that a corrosion rate can be electrochemically measured for a short time, quantification of corrosion rates is easy, and instantaneous corrosion rates can be obtained. This is, therefore, an extremely effective measuring method. The corrosion rate can be determined by measuring the polarization characteristics, for which a method to extrapolate a Tafel curve from the polarization characteristics of a comparatively wide potential area or a method to determine from the diffusion limiting current is available.

For electrochemical measurement, a test electrode, counter electrode, reference electrode, electrolysis vessel, power supply such as a potentiostat, and control device are used (Figure 3.1.39). For the counter electrode, platinum is used to meet requirements for both anodic and cathodic polarization and it is recommended to separate the counter electrode from the measuring chamber with a glass filter or other means to avoid influencing change in the liquid properties and evolved gas. For the reference electrode, calomel, silver-silver chloride, and copper-copper sulfate electrodes are used, which should be properly selected depending on the type of electrolyte of the measuring solution. In arranging electrodes in the electrolysis vessel, care must be taken to achieve as uniform a current distribution as possible on the test electrode and to bring the capillary tip end closer to minimize the measuring error of the polarization potential due to solution resistance.

Measurement of polarization characteristics falls into two broad categories: the controlled current method which brings the internal resistance of the measuring circuit to approach infinity with respect to the resistance in the electrolysis vessel, and the controlled potential method to bring it to a state of being infinitesimal. In general, polarization characteristics are frequently measured by the controlled potential method using a commercially available controlled potential electrolysis device: potentiostat. The reason is that this device is suited for measurement of the corrosion system: the capability to accurately measure polarization characteristics in a system in which the current varies negatively with respect to the potential, such as in passivation. Combining it with the dynamic potential equipment which can set various waveforms and varying speeds can easily produce polarization characteristics from transient response characteristics to a stationary state.

After an electrolysis vessel is filled with test solution and measuring conditions including temperature and ambient conditions are prepared, a test electrode is inserted and the corrosion potential is immediately measured. After this potential reaches the stationary state, cathodic, then anodic polarization characteristics are measured.

Tafel curve extrapolation method: In the corrosion system predominated by activation, the logarithm and the potential of polarization current form a linear relationship. This line is called the Tafel line, which can be extrapolated to the corrosion potential to determine i_{corr} . In this method, finding either the anodic or cathodic Tafel line enables the determination of i_{corr} in the same manner from the intersection of the line with the corrosion potential (Figure 3.1.40).

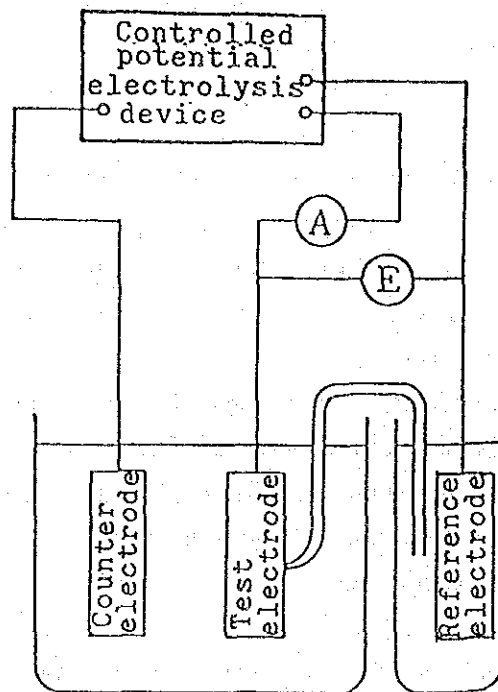


Fig.3.1.39 Block diagram for measuring controlled potential polarization characteristics ⁵

$$i = I_{\text{corr}} \exp(2.3 \Delta E/b)$$

Method to determine from diffusion limiting current:

The diffusion limiting current frequently observed in iron in a natural solution with dissolved oxygen is measured. In this event, the limiting current density coincides with the corrosion current (Figure 3.1.41).

Method to determine from passive current: In metal in a passive state, the passive current coincides with the corrosion current.

c) Polarization Resistance Method

The method to measure the polarization curve and extrapolate the Tafel line is most popularly applied for analysis of the electrode reaction mechanism, but it has many problems as a monitoring technique because current as large as 1000 times the corrosion current must be allowed to flow to obtain "linear portion," destroying the corrosion interface. Therefore, methods more suited for monitoring are proposed.

1) Linear Polarization Method (Direct Current Method)

This utilizes the phenomenon in which the polarization current I and polarization potential ΔE has a linear relationship at the low potential range polarization area (to 20 mV) in the vicinity of the corrosion potential, and the polarization resistance $\Delta E/I$ is inversely proportional to i_{corr} .

$$i_{\text{corr}} = K \frac{\Delta I}{\Delta E}$$

In general, instead of determining the Tafel coefficient, the corrosion current is found by measuring weight loss to determine proportional constant K and a corrosion rate is found from the relation of ΔE and ΔI of unsteady measurement.

There is a three-electrode method and a two-electrode method for measurement. The three-electrode method is used to determine the polarization resistance in the one-point measurement in the experimental range, after a saturated calomel electrode was experimentally used for a reference electrode, a platinum electrode was used for the counter electrode, and the linearity of the polarization curve in the vicinity of the corrosion potential of the sample electrode was tested. For the in-situ monitor gauge, probes using electrodes of the same shape, size, and material as electrode are generally used for the three electrodes. The two-electrode method consists of an electrode which serves both as a reference and a counter electrode and a test electrode, and the two electrodes are of the same shape, size, and material (Figure 3.1.42).

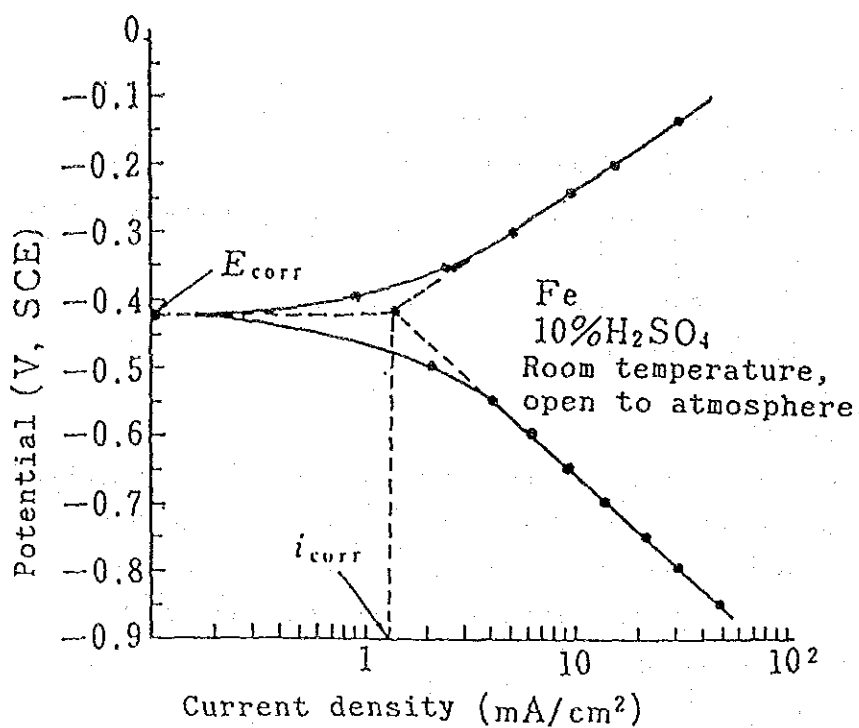


Fig.3.1.40 An example of measurement of corrosion current by Tafel extrapolation method ⁵

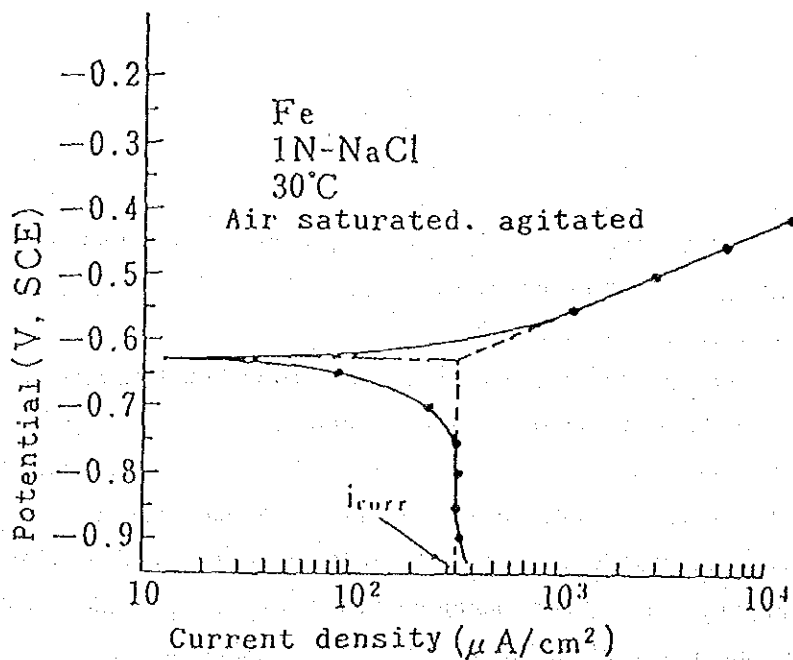
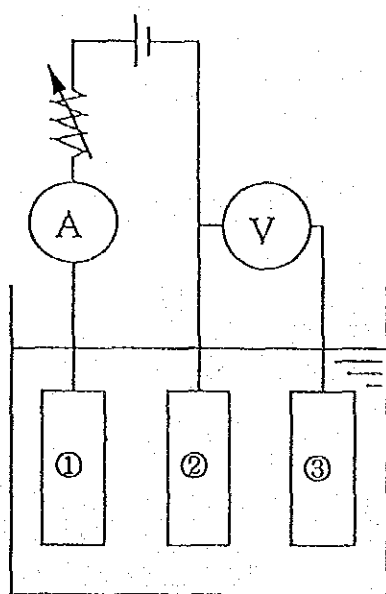


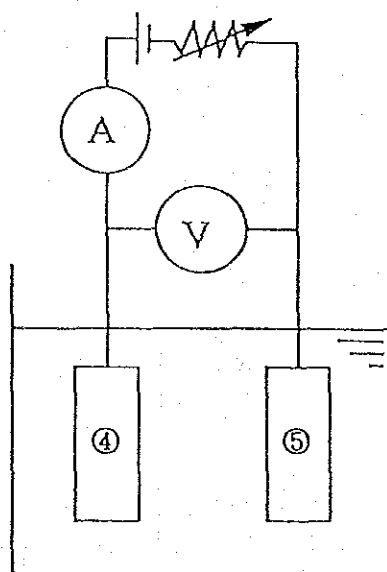
Fig.3.1.41 An example of measurement of corrosion current from diffusion limiting current ⁵

(a) Three-electrode method



- ① Counter electrode
- ② Test electrode
- ③ Reference electrode

(b) Two-electrode method



- ④ Test electrode
- ⑤ Test electrode

Fig.3.1.42 Electrode system and measuring apparatus ³⁹

Commercially available service gauges include the following: a. Corrosion Rate Meter (Petrolite Corp.), which employs the three-electrode method. It measures with either controlled current or by the controlled potential PAIR method, and indicate on the meter in mpy. b. Corra-tor (Magna Corp.). Except one type, all employ a direct method using two-electrode probes. c. RGY Testing Equipment. By varying the bath voltage of two sample electrodes from zero at a specified rate, the terminal voltage-current curves are determined and slopes at the curve origin are compared. This can be called a dynamic potential two-electrode method because the curve has linearity where terminal voltage is small. In the measuring apparatus (Corrorizer, Komyo Denki K.K.), a curve is measured by sweeping by 0-1.5 V and corrosion speed can be measured by sweeping in a range as small as 0-40 mV. d. Quick evaluation apparatus for metal corrosion rate (Toshiba Soken/Chemical Material Laboratory). Table 3.1.9 -3.1.12 show examples of experimental data exhibiting the relationship between the corrosion rate determined by the linear polarization method and that by other technique.

Table 3.1.9 Corrosion rate in Units 1 and 2 when iron is added(mpy, after J.A.Hanck et al.)⁴⁸

Test specimen	Condensed water	Linear polarization resistance method						Electri resista method
		Unit 1			Unit 2			
		Flow rate of condensed water (ft/sec.)						Flow ra .1-8 ft/s Unit 1 Unit 2
		1	8	8	1	8	8	
		Iron catalyst added						
not added	not added	added	not added	not added	added			
AISI 304	High temp	0.1-0.3	0.2-0.5	0.4-2.0	0.04-0.1	0.2-0.5	1-11	0.5-2.5
AISI 316	High temp	0.1-0.3	0.1-0.3	0.3-1.2	0.1-0.2	0.2-0.8	1-12	0.4-2.5
AA 6061	High temp	0.05-0.2	0.1-0.5	0.05-0.1	0.04-0.1	0.1-0.8	0.4-2	0.1-0.6
AA 3003	High temp	0.05-0.2	0.1-0.4	0.1-0.6	0.04-0.08	0.2-0.6	0.2-0.8	0.1-0.4
AISI 316	Low temp	0.02-0.06	0.02-0.04	0.04-0.1	0.02-0.06	0.05-0.08	0.05-0.2	<0.1

J. A. Hanck and G. Nekokse: Materials Performance.

15 (No. 7), 1976, p. 33.

Table 3.1.10 Results obtained in industrial cooling water system using a general-purpose corrosion rate indicator ⁴⁹

No.	Plant	Processing system	Processing standard		Corrosion rate (mpy)		Period
					Test specimen	Meter reading	
1	Glycol plant	Chromate system	CrO ₃ Ca	8~12ppm 600ppm, max	2.0~6.0	1.0~9.0	12 month
2	Oil refinery plant	Chromate system	pH CrO ₃ Ca	8.5 max 10~15ppm 600ppm, max	1.0~9.0	2.0~15.0	8
3	Oil refinery plant	Chromate system	CrO ₃ pH	10~15ppm 7.5~8.0	1.0~3.0	1.0~3.0	9
4	Air conditioner	Chromate system No. 1	CrO ₃ pH	80~120ppm 6.5~7.5	1.0~2.0	1.0~4.0	8
		Chromate system No. 2	CrO ₃ pH	5~10ppm 8.0~8.5	2.5~8.0	1.0~6.0	1.5
		Chromate system No. 3	CrO ₃ pH	45~50ppm 6.5~7.5	0.5~1.0	1.0~2.0	7
5	Gas cooler	Non chromate system	Total PO ₄ M alkalinity	8~10ppm 30~50ppm	0.5~2.0	1.0~2.0	4
6	Cold drawing	Non chromate system	Ortho PO ₄ pH Ca	2~4ppm 7.5~8.0 300 max	5.5~8.0	4.0~11.0	3
7	Engine test sand	Non chromate system	Total PO ₄ pH Soft water supply	6~10ppm 6.5~7.5	6.0~7.0	5.0~10.0	6
8	Furnace cooling	Non chromate system	Total PO ₄ pH Ca	4~6ppm 7.5~8.5 400ppm, max	6.0~10.0	4.0~9.0	4

D. Yamamoto: Corrosion Engineering (Boshoku Gijutsu).

28 (No. 3), 1979, p. 150-153.

Table 3.1.11

Comparison of corrosion rate at actual plants⁵⁰

(after J. C. Hill)

Inhibitor	Corrosion rate (mpy)	
	Test specimen	Linear polarization method
Chromate system	1.4	1.3
Low chromate system	3.0	3.3
"	3.0	2.9
"	10	12.1
Non chromate system	10	11.1
"	4.5	3.6
"	5.8	8.8
"	6.7	5.4
"	10	11.7
"	6.5	5.5
"	7.2	2.9
"	5.8	3.1
"	5.5	2.7
"	6.7	5.8

J.C.Hill:Preprint of Corrosion/1973 (NACE).

Table 3.1.12 Comparison of corrosion rate determined from linear polarization resistors and that of immersion test specimens at different places of a scrubber(carbon steel, stainless steel)(after P.A.Burda)⁵¹

Test specimen location	A ₀							
	One day				Six days			
	Weight loss (g)	Meter reading mpy	Proportional constant of probe (Ksp)	Meter reading mpy	Weight loss (g)	Meter reading mpy	Proportional constant of probe (Ksp)	Meter reading mpy
On a dewister (83 in. above M.B.)	0.04380	0.064	0.40	0.16	0.08100	0.025	0.49	0.05060
Marble bed	0.04600	0.084	0.34	0.25	0.03680	0.011	0.28	0.0395
SO ₂ inlet	0.17650	0.32	0.31	1.042	0.54200	0.17	0.23	0.70800
	A ₁₁				A ₁			
	Four days				Seven days			
	Weight loss (g)	Meter reading mpy	Proportional constant of probe (Ksp)	Meter reading mpy	Weight loss (g)	Meter reading mpy	Proportional constant of probe (Ksp)	Meter reading mpy
Below a dewister (83 in. above M.B.)	0.03310	0.015	0.44	0.3450	0.08230	0.022	0.72	0.02980
Marble bed	0.01950	0.0089	0.28	0.03180	0.19950	0.052	0.64	0.08190
SO ₂ inlet	1.93	0.88	0.27	3.27	0.0076	0.00070	0.18	0.03860
Reaction tank (Spray water)					0.29570	0.078	24.7	0.00314

* Erosion M.B.: marble bed
 1131655 A₀, A₁₁, A₁ - Test conditions

P. A. Burda: Materials Performance, 14 (No. 6), 1975, p. 27.

Test period: 20 days

2) AC Impedance Method

The AC method is one of the typical non-stationary methods used in electrochemistry. Since a stationary value with respect to AC is used for measurement, analysis and measurement tend not to be so difficult. However, an erroneous conclusion may sometimes be drawn.

The gradient of a stationary current-potential curve at $E=E_{\text{corr}}$ corresponds to the polarization resistance R_p . Measurement by the AC method is to determine the differential value $(di/dE)_{E=E_{\text{corr}}} = 1/R_p$ of the current-potential curve at E_{corr} . Impedance Z cell at each frequency is measured and is plotted on the complex plane with the frequency as a parameter. Then, R_p is found by using the equivalent circuit as shown in Figures 3.1.43 and 3.1.44.

$$(Z' - R_{\text{sol}} - R_c/2)^2 + (Z'')^2 = (R_c/2)^2$$

In measuring, when a test electrode is controlled-potential-polarized, AC voltage is overlapped by the set potential of the potentiostat. For the corrosion potential, a handy technique by the two-electrode method is applicable (Figure 3.1.45). To determine the amplitude ratio and phase difference, a lock-in-amplifier is used. Figure 3.1.46 shows one example of data exhibiting the relationship between the corrosion rate measured by the AC impedance method and the weight loss of various metals under various environments.

3) Coulostat Method

The coulostat method refers to a technique designed to regulate the electric charge (Coulomb), whereas the potentiostat and galvanostat methods are techniques to regulate the potential and the current, respectively. The coulostat method provides a microelectric charge to the electric double layer of specimen metal using an external power supply, and measures the recovering process of the potential which is shifted by the electric charge. This will determine the polarization resistance R_p and i_{corr} is found.

To measure, a device shown in Figure 3.1.47 is used and the process is recorded in a synchroscope or digital memory as an overvoltage curve. Table 3.1.13 summarizes examples of experimental data exhibiting the relationship between the corrosion rate factors determined by the coulostat method and those determined by the conventional methods. The values determined by both methods show comparatively good agreement, suggesting usefulness of the coulostat method.

4) Current Interrupt Method

Using a rectangular-wave-controlled current generating apparatus, controlled current of the rectangular wave with positive-negative symmetry and duty ratio 1 is applied to the corro-



Fig.3.1.43 Equivalent circuit of corroding electrode ⁴⁷

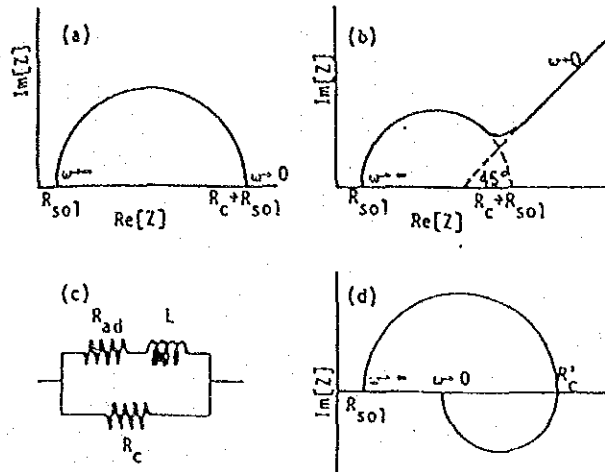


Fig.3.1.44 Impedance locus chart of various corrosion reactions ⁴⁷
 Equivalent circuit (c) of reaction resistance when (a), (b), (d) and inhibitor are included.

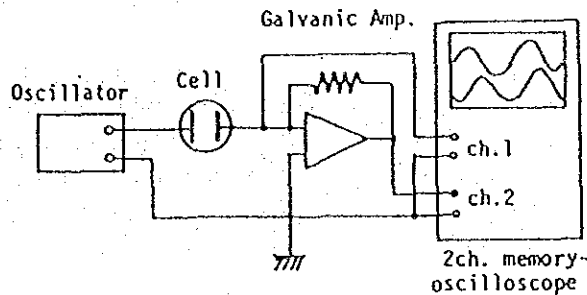


Fig.3.1.45 Example of measurement circuit for AC method using 2-electrode method ⁴⁷

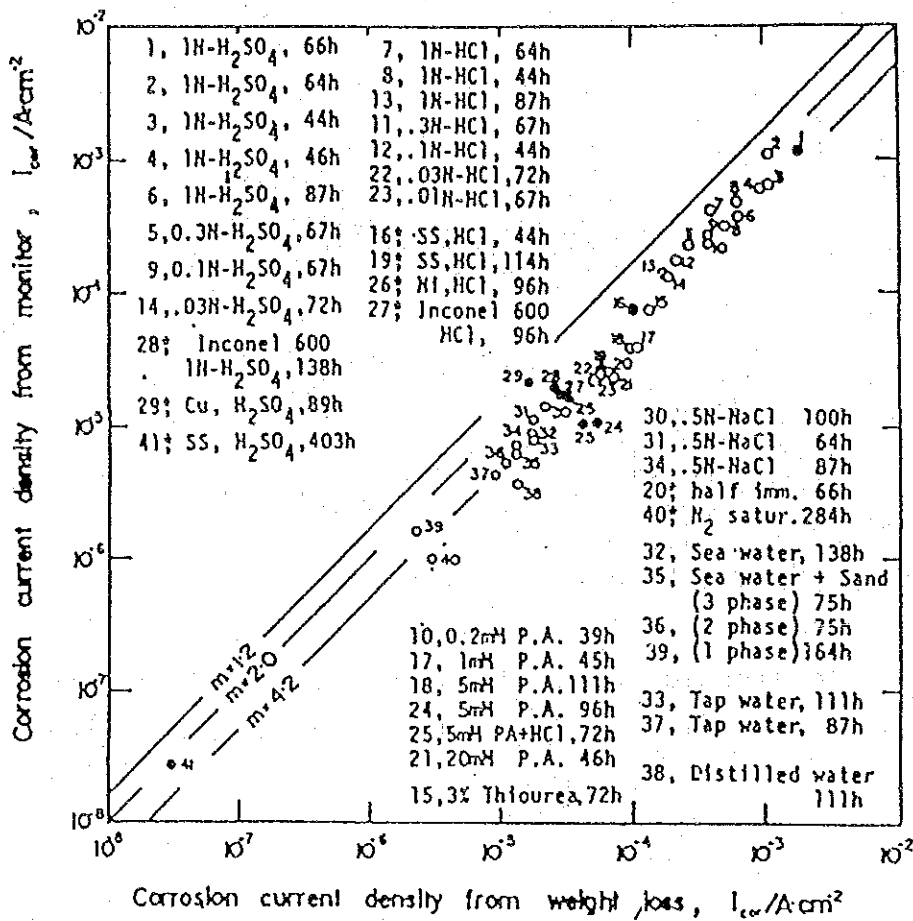


Fig.3.1.46

Relationship between monitored corrosion rates by the AC impedance method and corrosion losses of various metals under various environments⁴⁷

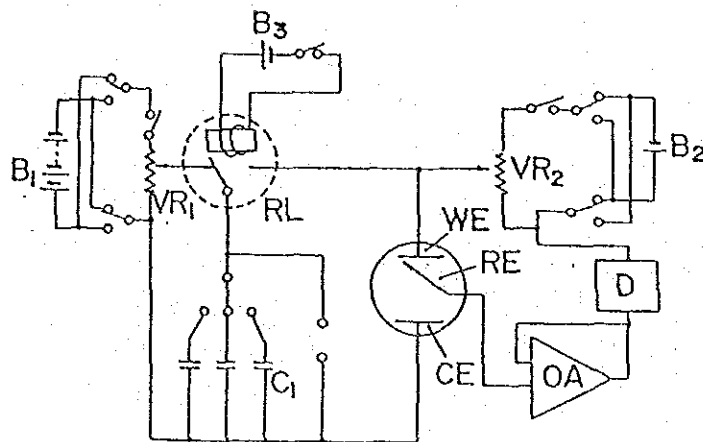


Fig.3.1.47 Block diagram of coulostat equipment⁴⁷
 WE: test electrode, RE: reference electrode,
 CE; counter electrode, OA: operational
 amplifier, D: voltage recorder, C₁: condenser
 to provide charge to WE

Table 3.1.13 Relationship between corrosion rate factors determined by the coulometric method and by the conventional polarization resistant method ⁴⁷

Measuring system (Metal, test solution)	t, hr	Coulometric method					Conventional method			
		C _i μF/cm ²	β _a mV	β _c mV	R _p Ωcm ²	I _{corr} μA/cm ²	β _a mV	β _c mV	R _p Ωcm ²	I _{corr} μA/cm ²
Pure iron 1N H ₂ SO ₄ (Oxygen removed by N ₂)	4	39.2	65	115	89	200	52	138	99	170 ^{*1}
Carbon steel distilled water (SS41)	91	74.9	76	63	2.5 × 10 ³	6.0				
	259	127	57	50	1.4 × 10 ³	8.2				10.6 ^{*2}
Carbon steel 1N H ₂ SO ₄ (SB46)	2	216			7.9		51	128	5.6	2.8 × 10 ^{3*}
SUS304, 1N H ₂ SO ₄	28	55.0			430 × 10 ³	5.1 × 10 ⁻¹			540 × 10 ³	4.0 × 10 ^{-2*}
	54	50.4			610 × 10 ³	3.6 × 10 ⁻¹			720 × 10 ³	3.0 × 10 ⁻²
SUS304, 10% FeCl ₃	2	41.0			1.4 × 10 ³					
	19	39.2			1.4 × 10 ³					3.1 × 10 ^{3*}

Unless otherwise specified, measurement was performed under open atmosphere.

- *1 Immersion time
- *2 from polarization curve
- *3 Weight loss method
- *4 Calculated from passivity holding current in +0.48V vs. SCE (β ...)
- *5 Weight loss method (let β_a = 90 mV, ...)

sion system and the potential response to this is recorded by the recorder after biasing and extending. Measurement is carried out with 0.01 Hz applied current at which the potential response becomes nearly stationary. Separately, 100 Hz rectangular wave controlled current is applied and the solution resistance is found from the sharp leading edge. Removing the solution resistance E_s from the former potential response E_{p-p} , polarization resistance R_{corr} is found (Figures 3.1.48 and 3.1.49).

$$R_{corr} = \frac{\Delta E}{2\Delta I} S = \frac{\Delta E_{p-p} - \Delta E_s}{2\Delta I} S$$

3.1.3 Test Equipment on Actual Plant Level

(1) Loop Test ⁵⁵⁻⁵⁷

In general, in selecting materials for plants, it is recommended to install test specimens in the actual equipment or pilot plants and to confirm the corrosion resistance. In order to develop materials for heat exchanger tubes used in MSF seawater desalination plants in Japan, in 1967 loop test and field test plants were constructed at the Seawater Desalination Seaside Research Facilities of the Tokyo Industrial Research Institute in Chigasaki. We believe that these plants and experimental processes might be helpful in proposing a construction plan for higher performance on-line level test plants and hope to provide some of the information on them. First of all, discussion is made on the loop test equipment of the Tokyo Industrial Research Institute.

Figure 3.1.50 shows a flow sheet of this loop test plant. There are three circulation loops, A, B, and C, and the test section of each loop consists of two pieces of titanium pipe. To the C loop, a device to add magnesium hydroxide species is attached to hold the pH of the circulating brine to extreme environmental conditions of around 9. The operation variables are 70–125°C for temperature, 1–3 m/sec for flow rate, 1–2 for seawater concentration, pH 4–7 (4–9 for C loop), and 10–200 ppb for dissolved oxygen. The brine supply ratio is 5% (250 kg/hr of brine supplied for a 5000 kg/hr circulation rate), 20–30% less than that used in multi-stage flash equipment.

For the construction materials of the apparatus, primarily plastics such as polycarbonate and various organic lining steels are used for the low-temperature section and titanium is primarily used for the high-temperature section to minimize contamination of brine due to metal dissolution.

With respect to specimens, plate type specimens shown in Figure 3.1.51 are used. Their size is 30 x 60 x 2 mm and 28 pieces of such specimens are arranged in two rows in a titanium tube holder with Teflon as insulation material. In 1971, the brine heaters of loops A and B were

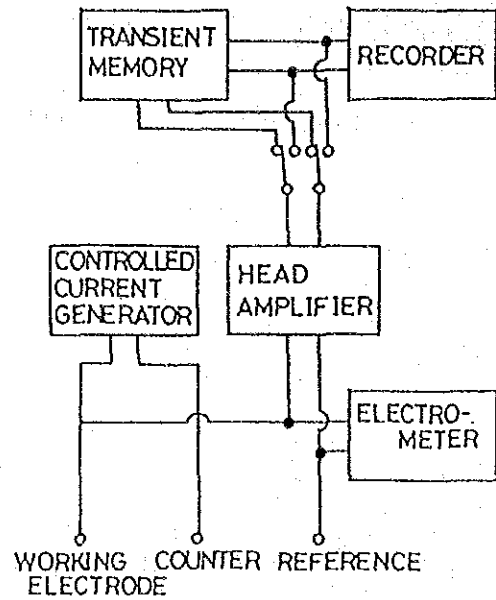


Fig.3.1.48 Block diagram of polarization resistance measuring apparatus⁵⁴

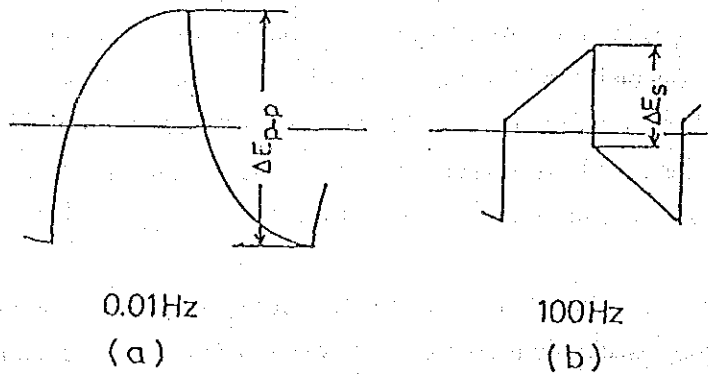


Fig.3.1.49 Typical potential response waveform⁵⁴

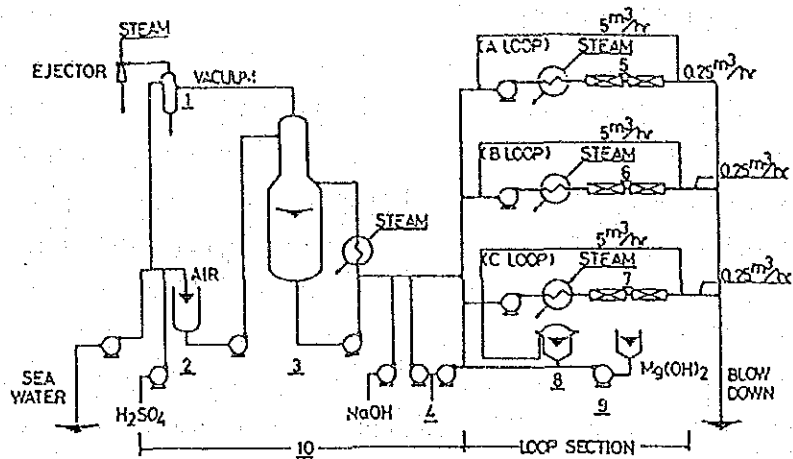


Fig.3.1.50

Simplified flow sheet of loop test plant.

1: barometric condenser, 2: decarbonator, 3: deaerator and concentrator, 4: O₂ saturated sea water, 5: test section A, 6: test section B, 7: test section C, 8: thickener, 9: alkali control section, 10: pretreatment section. ⁵⁵

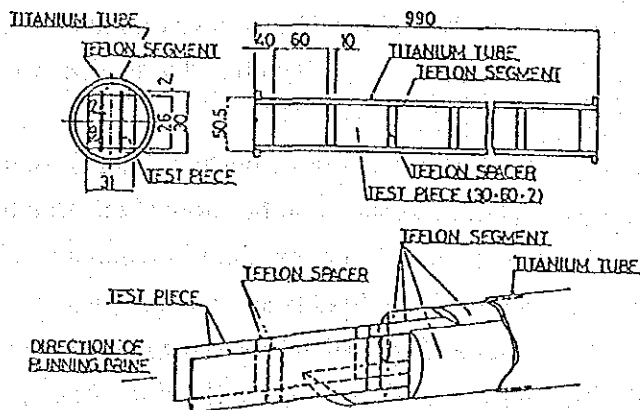


Fig.3.1.51

Test specimens and holder in test section of loop test plant. ⁵⁵

modified to act as a heat exchanger tube replacing system. Figure 3.1.52 shows the construction. Four pieces, each of 17.3 x t x 1 280 mm (t = 0.3 and 1.2) heat exchanger tube per one loop totalling 8 pieces, were installed by a ferrule system and were tested as tubes placed under heat transfer conditions, which reproduced more practical conditions.

The experiment using this apparatus was commenced in 1970 and a total of 17 test runs, with one run comprising 1000 hours, were performed before the experiment was ended in 1972. A wide variety of materials, corrosion rates by weight loss, characteristics of pitting and crevice corrosion, and scale adhering speed were determined, and based on the test results, materials for heat exchanger tubes were selected for the field tests, which were commenced from 1971.

Then, as another example of the loop test plant, a flow sheet of the pilot test loop comprising glass-PTFE fabricated by Manner et al. is shown in Figure 3.1.53. Figure 3.1.54 shows the detailed schematic diagram. The operation variables are 40-120°C for temperature, 0-2 m/sec for flow rate, pH 8.2±0.2, and 2-100 ppb for dissolved oxygen. Figure 3.1.55 shows the profile of the specimen used in this experiment. For the specimen holder, glass fiber reinforced epoxy resin (Figure 3.1.56) and glass-PTFE (Figure 3.1.57) are used. The results were evaluated by the mass reduction method and electrochemical method.

(2) Field Test⁵⁵

A field test plant is introduced. This plant was constructed at the seaside research facilities in 1970 and experiments were carried out from 1971 to 1973 under the conditions closer to those of the actual equipment than in loop tests.

The plant is a short-tube type multistage flash evaporator with a fresh water production rate of 24 m³/d. The flow sheet is shown in Figure 3.1.58, plant design specifications in Table 3.1.14, and the general view in Figure 3.1.59.

To this plant, heat exchanger tubes (about 160 pieces at a time) made from the materials selected on the basis of the loop test results were installed and tests were carried out under conditions simulating nearly actual conditions.

The major section of the plant consists of brine heaters, a heat recovery section (4 stages) and a heat rejection section (two stages), as shown in the flow sheet. Due to the peculiarity as a heat exchanger tube test plant, lines A and B are arranged in parallel as a heat exchanger tube bundle of the heat recovery section and brine heaters and are designed to carry out tests on different types of materials on both lines and with slightly varying operating conditions.

The specimen tube bundles are all designed as a floating head type, enabling easy replacement of heat exchanger tubes for each test run. The heat exchanger tubes are, in general, installed to the tube sheet with a flare pipe, but a ferrule system was employed for the coated materials. For the construction material of the overall plant, carbon steel is employed for almost

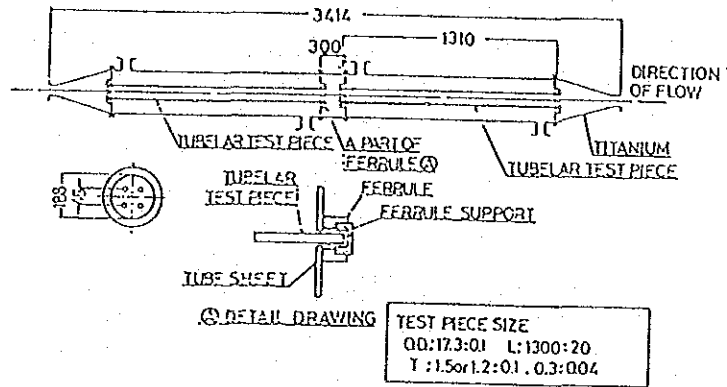
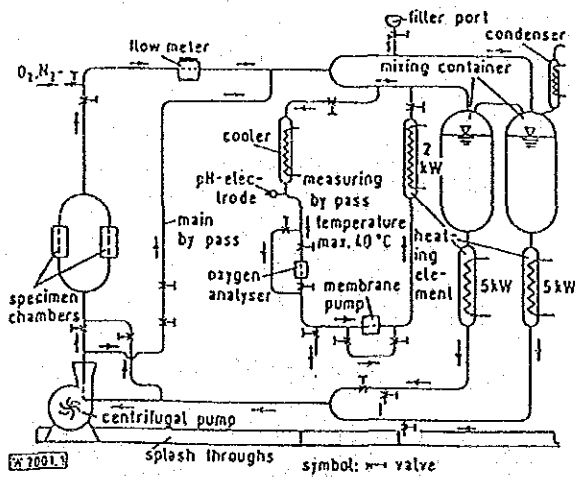


Fig.3.1.52 Test tubes in brine heater of loop test plant. ⁵⁵



Simplified flow sheet of the pilot test loop
Vereinfachtes Fließschema des Pilot-Prüfkreislaufs

Fig.3.1.53 Simplified flow sheet of the pilot test loop ⁵⁶

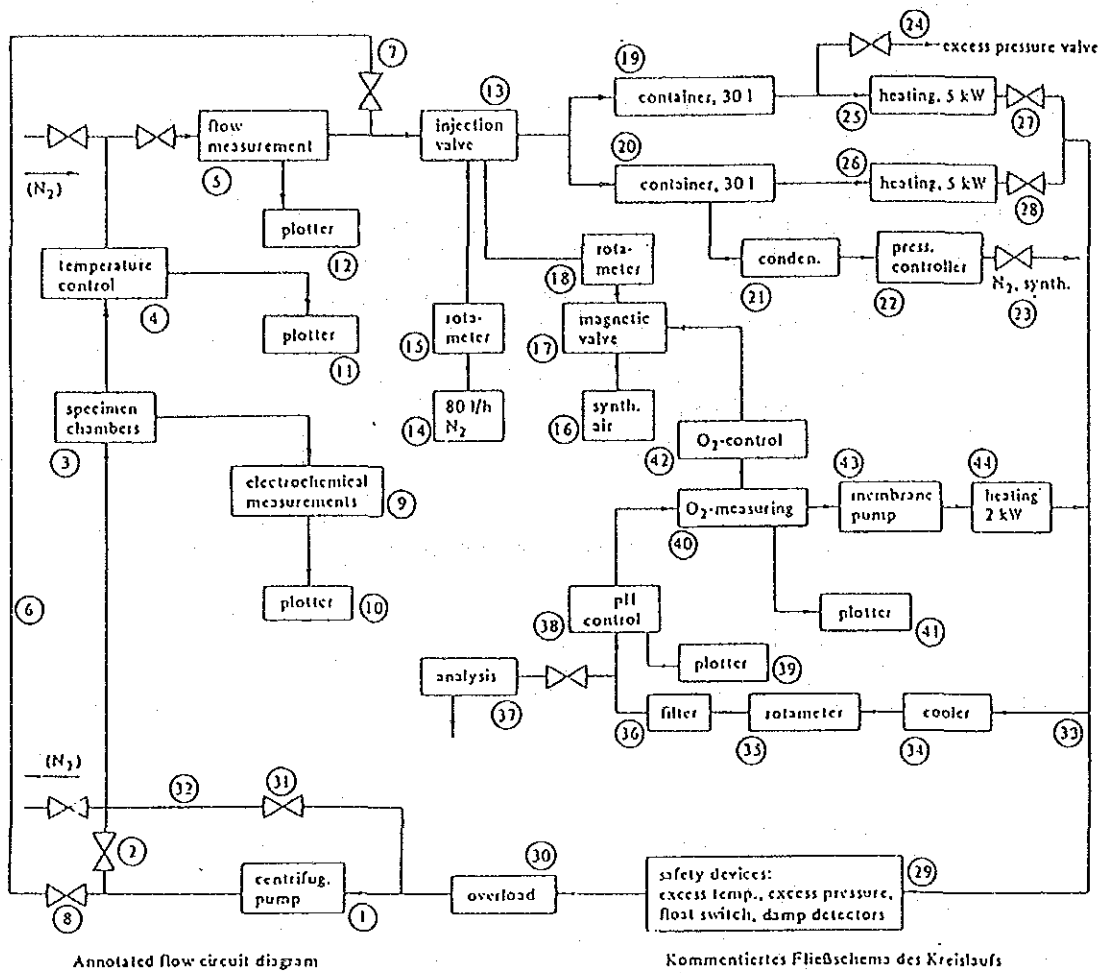
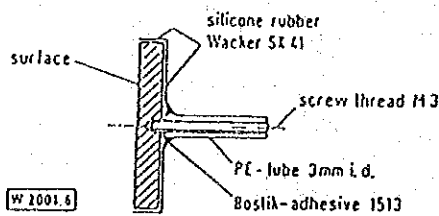


Fig.3.1.54 Annotated flow circuit diagram ⁵⁶



Cross section of a coated specimen
 Schnitt durch die Probenabdeckung ⁵⁶

Fig.3.1.55

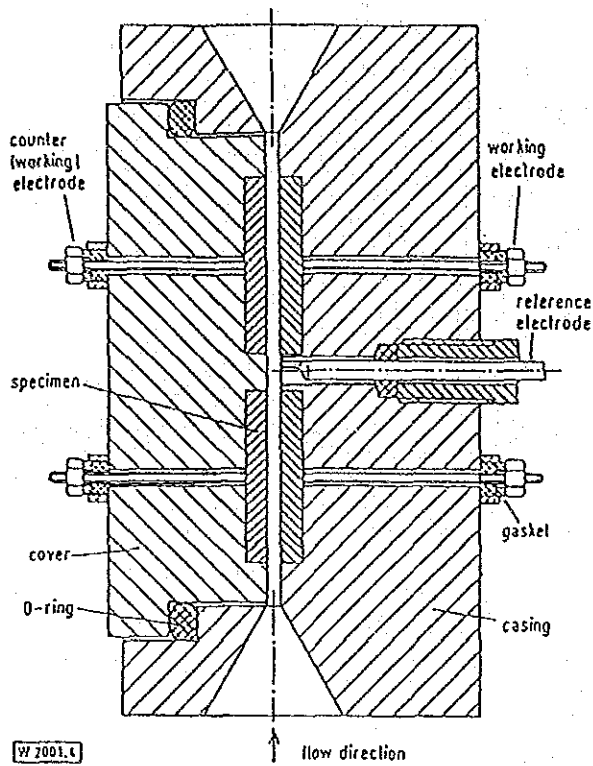


Fig.3.1.56
Specimen chamber constructed
from glass fiber reinforced
epoxy resin ⁵⁶

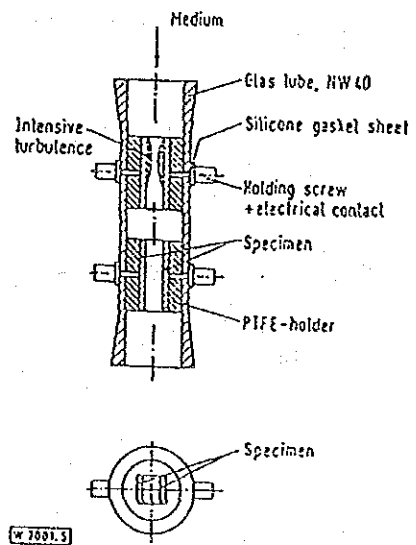


Fig.3.1.57
Specimen chamber constructed
from glass and PTFE ⁵⁶

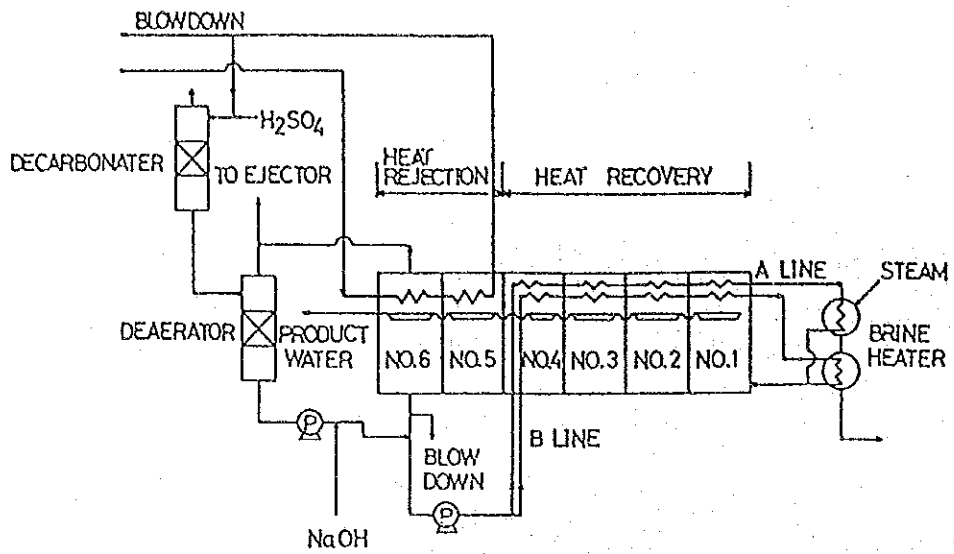


Fig.3.1.58 Simplified flow sheet of field test plant.⁵⁵

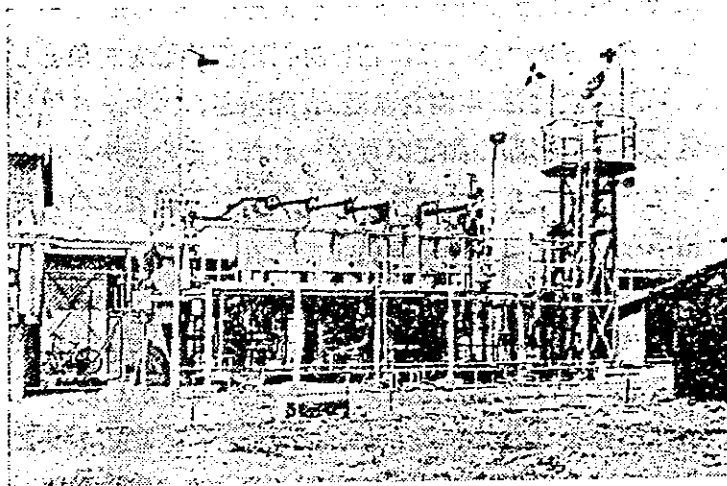


Fig.3.1.59 Field test plant.⁵⁵

Table 3.1.14 Design parameter of field test plant. ⁵⁵

Unit	
Number of stages	heat recovery: 4 heat rejection: 2
Circulating brine requirement	7 m ³ /hr × 2
Sea water (make-up) requirement	2.4 m ³ /hr
Range of temperature (circulating brine)	120°C-67°C
Range of temperature (cooling water)	45°C-25°C
Velocity (in condenser tube)	1.8 m/s
Output, distilled water	1 m ³ /hr (24 m ³ /d)
Steam requirement	0.7 T/hr (10 kg/cm ²)
Brine pH	7
DO in brine	< 10 ppb
Performance	2 (kg·fresh water/ kg·steam)
Tube bundle	
Size of tubes	: 19.05φ × t × 2,000-2,500 (brine heater) ferrous, t: 1.5, nonferrous, t: 1.2, 0.3 (Ti)
Type of tubes	: brine heater: 4 path × 2.5 m 1 (path consists of 6 tubes) heat recovery: 2 path × 2 m (1 path consists of 5 tubes) heat rejection: 2 path × 2 m (1 path consists of 12 tubes)
Number of bundle	: brine heater: 2 series heat recovery: 4 stage × 2 series heat rejection: 2 stages

all parts of the plant, with stainless steel for some parts, in view of the actual state of a large-size plant. In the flow sheet, a deaerator is shown. From the very beginning of Run 0, external deaeration was performed by this deaerator, but after 1000 hours of Run 6, it was modified to carry out the final deaeration at the sixth evaporation chamber of the heat rejection section. In this case, air in the steam phase of the sixth stage increases, accelerating corrosion on the outer surface of the tube depending on the material.

In order to investigate the operation to qualify the property and performance of the plant and the analytical method of the corrosion conditions of tubes, Run 0 was performed first. Then, in order to further narrow the material, Run 1, 2, 3 were carried out as screening tests, and in Run 4, designed as a service test, effects of operating conditions on the corrosion and overall heat transfer coefficient were investigated. In Run 5, effects of the insulation method between the aluminum alloy tube bundle and the steel structure proper were investigated. In the final Run 6, one piece each of heat exchanger tube made from copper alloy, low alloy steel, stainless steel, and titanium, which were selected as standard materials (a total of 4 types), were installed and long-term tests were performed. The operating time for one run was normally 2000 hours, but Run 6 was designed to produce data for a total of 5000 hours for every 1000 hours.

A large part of the heat exchanger tube material which underwent the final test was selected on the basis of the screening results of loop tests, but there were cases, such as carbon steel, in which materials were selected for comparison criteria for the specific material group in spite of their large corrosion rates.

For the material of the tube sheet, the following were used to meet the properties of the heat exchanger tube materials, but of these, in the case of the aluminum alloy tube bundle, insulation was provided between the steel structure and water box to prevent galvanic corrosion.

As a result of the experiments using these plants, evaluation was carried out on various heat exchanger tube materials.

3.2 Proposal of a Design Plan for a Corrosion Evaluation Test Plant for Research on Corrosion-resistant Materials related to SWCC Seawater Desalination

3.2.1 Laboratory Level Testing Apparatus⁵⁸⁻⁶²

Since the laboratory level testing apparatus forms the basis of electrochemical or corrosion engineering studies, as many apparatus as possible should be accommodated. Of all the tests, the immersion type test (3.1.1.-(1)) is the most fundamental, and it is recommended that as many corrosion cells as possible including thermostats, be prepared, ranging from simple beakers to those with good temperature controlling accuracy so that tests can be carried out at any time.

In this case, measuring or regulating the specimen potential is important not only for

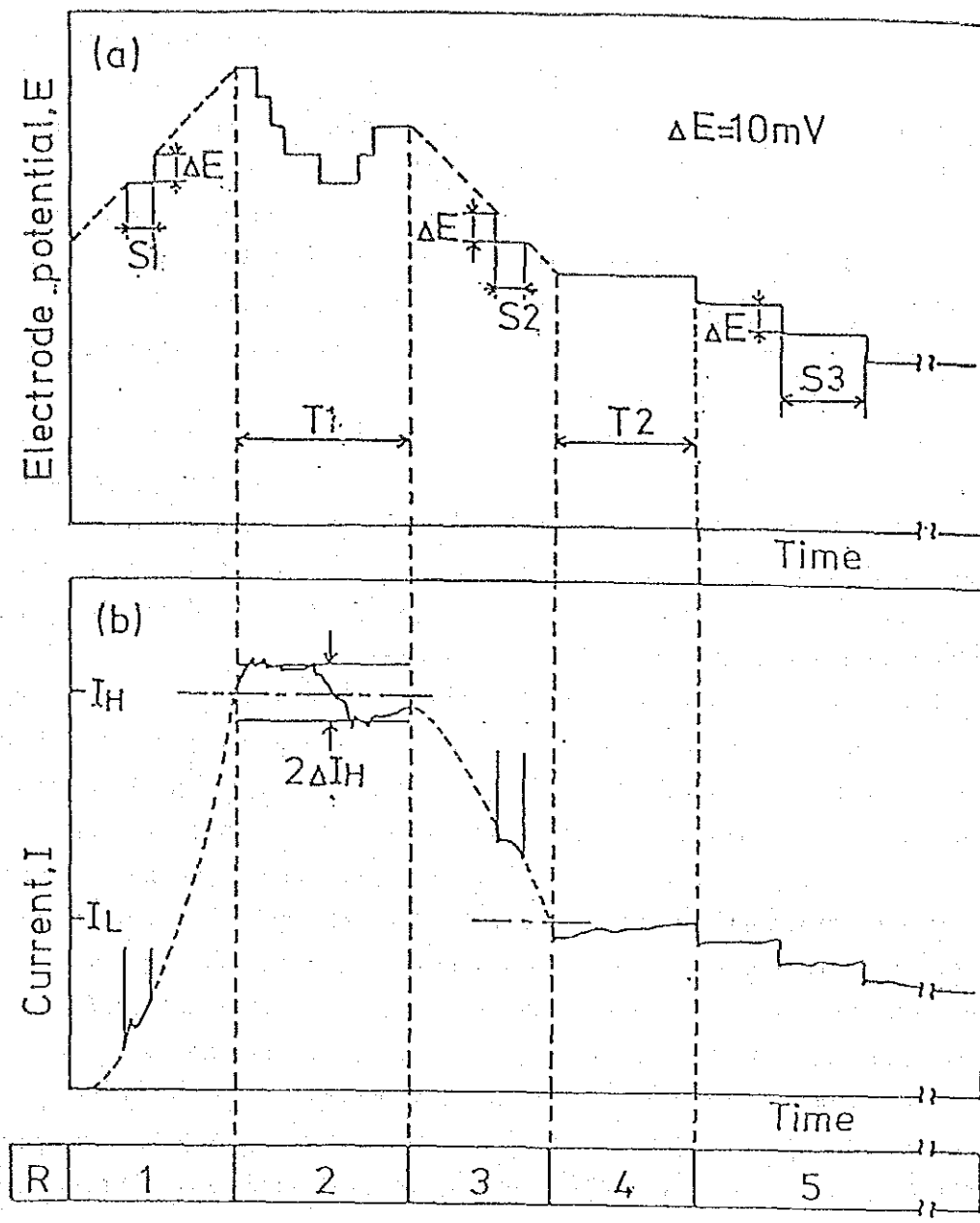


Fig.3.2.1 Potential operation (a) and current change (b) when repassivation potential (E_R) is measured.⁵⁸

electrochemical and corrosion engineering research but also for understanding corrosion behavior. It is, therefore, recommended to procure a wide variety of electrometers and potentiostats (potentiostats which cost less than 100,000 yen are commercially available in Japan).

Stress corrosion cracking (SCC) in stainless Steel often initiates from localized corrosion such as pitting or crevice corrosion in a nearly neutral chloride environment such as seawater or fresh water, and the conditions of its occurrence can be arranged by the "dissolution and cracking rate competing concept" (when a cracking rate is greater than a dissolving rate, SCC occurs). Consequently, from their critical potentials (pitting potential V_c and crevice corrosion potential V_{crev}), the lower limit potential of SCC can be found.

Comparison with the potential measured in actual equipment enables prediction of the possibility of localized corrosion occurrence. That is, if the corrosion potential is located on a much less noble side than the critical potential, it can be judged that there is no possibility of localized corrosion occurrence. Even in such critical potential measurement, the potentiostat becomes a useful measuring device. In general, the potentiostat operating on the dynamic potential method (V_c' and V_{crev}') is used.

In the actual equipment, crevice corrosion which may initiate and grow even under a mild environment tends to constitute problems, and V_{crev} measured by the controlled potential method is recommended for the evaluation. The less noble the potential, the longer the time required before crevice corrosion occurs. When the potential becomes less noble than the critical potential (V_{crev}), crevice corrosion will not occur even after a long time. However, with an increase in corrosion resistance of the material, the time required for determining V_{crev} increases, generating a new problem; how much time should be taken for testing. Even if any crevice corrosion did not occur in controlled potential tests up to 1000 hours (about 40 days), it does not mean that crevice corrosion will not occur in one year or more.

Some groups of researchers have advocated the repassivation potential E_R or $E_{R,crev}$ to escape the restriction of test time. Figure 3.2.1 shows a schematic diagram of changes of potential (Figure (a)) and current (Figure (b)) with time when ER is measured. At first, the potential is swept gradually to the noble side (ex. 10 mV/10 min) and crevice corrosion is allowed to occur (Stage 1). Crevice corrosion is generated at the point where specimen current exceeds the specified value (I_H), and thereafter keeping the current nearly to I_H , crevice corrosion is allowed to grow (Stage 2). In the range where there is no fear of interrupting the growth of crevice corrosion, the potential is swept to the less noble direction relatively rapidly (ex. 10 mV/10 min) (Stage 3), and after current becomes smaller than a specified value (I_L), the potential is swept to the less noble direction slowly (ex. 10 mV/60 min) (Stages 4 and 5). Let the most noble potential be E_R , in which the specimen current is negative and does not increase in the anodic direction. E_R is equal to V_c and is the characteristic value for the combination of material and envi-

ronment (Cl^- concentration, temperature, etc.) which can be found irrespective of crevice geometry or surface conditions. An automatic polarization apparatus combining a potentiostat and microcomputer and including the ER measuring software is commercially available.

The method to evaluate crevice corrosion resistance of metallic materials using $E_{R,CREV}$ was developed and advanced in Japan. That is, if the corrosion potential (E_{CORR}) of material is less noble than $E_{R,CREV}$ under the service environment, it can be asserted that crevice corrosion will never occur under these conditions and, if it is nobler, the crevice corrosion may occur. This kind of technique is believed to be useful to understand the critical corrosion resistance conditions of passive metals such as stainless steels, titanium materials, and nickel-based alloys which are used under a chloride environment. As an application of this technique, a technique to directly determine the applicable limiting temperature ($T_{R,CREV}$) and applicable limiting concentration ($C_{R,CREV}$) for crevice corrosion is being established.

Keeping the specimen to the controlled potential nobler than the above-mentioned critical potential (V_c or E_R), or keeping the specimen to the specified controlled potential after pitting or crevice corrosion is allowed to occur, load is applied to carry out the SCC test. Even if pitting or crevice corrosion is taking place, unless SCC is observed, there is no fear of SCC occurrence under the combination of the material and the environment. With respect to SCC which is initiated from pitting, load is applied to smooth specimens such as round bars or wire by a creep testing machine and springs. For the SCC which is initiated from crevice corrosion, load is applied to creviced round bar specimens⁵³ or fracture-mechanical specimens⁵⁴. In view of the handiness of tests, a spot-welded specimen⁵⁵ developed in Japan (Figure 3.3.2) with a crevice structure and residual stress is effective.

For other facilities, investigation should be made in reference to Section 3.1.1. If we were to decide the ranking of facilities, it would be better to select the corrosion testing apparatus under heat transfer and repeated dry and wet testing apparatus first, which would provide the environment of seawater desalination plants. Unless mud or sand or bubbles in sea water is excessively severe, corrosion accompanied by mechanical action will not occur so frequently.

3.2.2 Corrosion Monitoring Apparatus

The mass reduction measuring method is the most fundamental method to determine the corrosion rate as far as general corrosion is concerned, and can be easily carried out if a chemical balance or an electronic balance equivalent to the chemical balance (resolution: 1 mg or 0.1 mg or so) is available.

Measurement of thickness enables in-situ measurement of erosion depth and would be one of the outstanding methods for monitoring. Of all methods, the ultrasonic wave method requires the smallest equipment, is easy to handle and is comparatively inexpensive. This should be included in the proposed equipment list. The same principle applies to the eddy current flaw

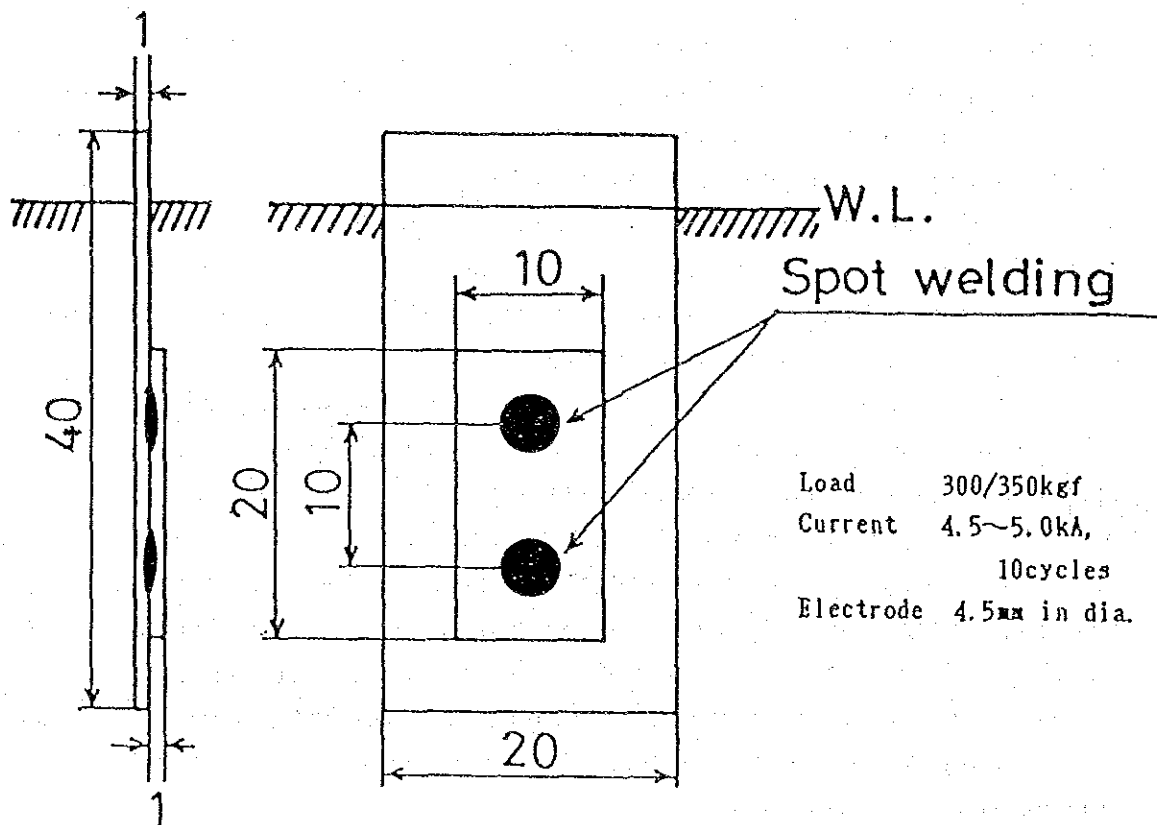


Fig.3.2.2 Spot welded specimen for crevice corrosion test ⁶²

detector. The chemical analysis measures the corrosion rate as a dissolved ion rate. It is not possible to determine the corrosion site but the generation and propagation status of corrosion can be determined. The ion electrodes are available with many types of sensors for both anion and cation. Combined with regular recording equipment or a recording device operating in linkage with a computer, measurement in-situ is possible. As far as cation is concerned, if continuous measurement is not needed, an ICP emission spectrophotometer can be applied. This equipment provides high sensitivity and a wide measuring range.

As an electrochemical method, the electrode potential method is the easiest and most basic method, and by comparison with the above-mentioned critical potential, the possibility of the occurrence of localized corrosion can be evaluated. Because the potential becomes less noble when corrosion initiates (because the cathodic current, which corresponds to the anodic current accompanied by the initiation of corrosion, is allowed to flow), monitoring of corrosion initiation is possible. The polarization resistance method can determine the corrosion rate as far as general corrosion is concerned. Of all, the measuring equipment for the AC impedance method is commercially available from many manufacturers in various countries and is considered very useful equipment.

3.2.3 Test Equipment on Actual Plant Level ⁵⁶⁻⁵⁷

Loop tests should be carried out to perform corrosion tests involving the flow of the solution. The field test is recommended for evaluation with temperature and ion concentration involved. In such a case, installing not only specimens but also the above mentioned monitoring equipment enables further detailed investigation on corrosion behavior.

In order to estimate the maximum pitting depth that causes water leakage in on-line equipment, extreme-value statistics (Gumbel distribution) are often employed. Methods to predict corrosion life fall into two broad categories: 1) the definitive theory method and 2) the probability statistics method. This section outlines the probability statistics method which has recently been widely used in Japan. Corrosion life is discussed using heat exchangers comprising a large number of heat transfer tubes as an example. Even if heat transfer tubes manufactured from the same material are used and the environmental conditions are the same, the life of each heat transfer tube varies scattering. The life of a heat exchanger as a system is determined by the shortest life value of the heat transfer tubes, and in this case, it is necessary to estimate the minimal value of the life distribution of heat transfer tubes. It is the extreme statistics which designate the maximum penetration depth in pitting and the minimal value in the life to an extreme value as a whole and estimates its distribution, that is, the properties of extreme value distribution and the distribution parameters. It is known that if the maximum penetration depth of corrosion is X , the cumulative distribution function $F(X)$ complies with the following Gumbel