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EXPERIENCE WITH HYDROGEN ADDITION WATER CHEMISTRY IN THE FUGEN NUCLEAR POWER STATION

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Long term trends in water chemistry have been appeared in the Fugen after more than two years' hydrogen water chemistry : an increase of soluble Co-60 concentration and cyclic concentration change of Cr-51 in reactor water, an increase of soluble iron concentration in condensate, and acceleration of radioactivity buildup on pipeworks in the reactor cooling system. The hydrogen addition has been carried out using hydrogen produced by a water electrolysis system on the site. Protective effect of hydrogen addition on mitigating the IGSCC susceptibility of Type 304 stainless steel is maintained. Hydrogen uptake by zircaloy-2 is not accelerated with the hydrogen addition.

INTRODUCTION

Continuous hydrogen addition has been implemented in the Fugen since December 1985 as a countermeasure against the stress corrosion cracking of Type 304 stainless steel after the in-reactor test carried out as previously reported (ref. 1). The hydrogen addition technique becomes very popular among American and Swedish nuclear power plant and its effectiveness on mitigating IGSCC has been proven (ref. 2-4). The studies on secondary effect of the hydrogen addition technique, especially on radioactive corrosion product change, are under way because the change occurs after long term plant operation. Authors report the secondary effect of the hydrogen addition water chemistry in the Fugen. The intermediate results of material test carried out after the in-reactor test previously reported are also described.

PLANT DESCRIPTION

General

The Fugen is a 165MWe prototype of the heavy water moderated, boiling light water cooled, pressure tube type reactor using uranium-plutonium mixed oxide fuel. The Fugen came into its commercial operation in March 1979 and has operated for over 1800 effective full power days (ref. 5).

A schematic diagram of the primary cooling system is shown in Fig. 1. Fuel assemblies of 224 are separately loaded in each pressure tube which is located through a calandria tank filled with heavy water. Light water introduced to the core cools the

fuel assemblies and changes into two phase flow (285°C, 68kg/cm²). Two steam drums separate the high temperature two phase fluid into water and steam. The water is recirculated at 8800 t/h and purified with two deep bed type demineralizers at 60 t/h of flow rate. The steam rotates a turbine generator and changes to condensate which returns to the core as feed water at 910 t/h flow rate after purified with four deep bed type demineralizers.

Gas supply system

A hydrogen and oxygen generating system was constructed at the Fugen site in December 1985. A schematic diagram of the system with three water electrolyzers is shown in Fig. 2. The system dissociates 30 wt% of KOH solution into 30 Nm³/h of hydrogen and 15 Nm³/h of oxygen at the maximum rate using two of the three electrolyzers. Each electrolyzer has 64 cells fabricated in series. Rated electric power consumption is 600 A of direct current at 130 V an electrolyzer. Hydrogen is compressed to 32 kg/cm² and injected to the feed water system. Oxygen generated with the electrolyzer at 5 kg/cm² flows into off-gas system to recombine the excess hydrogen extracted from main condensers. The hydrogen and oxygen are kept their purity over 99.9 % and 99 %, respectively. Flow rate of hydrogen is controlled in proportion to the feed water flow rate. Oxygen flow rate is kept at 60 % of hydrogen flow rate. The oxygen flow rate increases as soon as the hydrogen flow rate increases, but contrarily the oxygen flow rate reduces 30 minutes later after reduction of the hydrogen flow rate to recombine the excess

hydrogen entirely since the time requires 4 - 5 minutes that the hydrogen reaches to the oxygen injection port of the off-gas system. The hydrogen and oxygen generating system avoided labors with gas cylinder exchange and traffic difficulties with cylinder transportation.

The oxygen injected to the feed water line as shown in Fig. 1 is supplied from small cylinders at the flow rate of 10 l/h to prevent the feed water line from iron release, to restrict iron transport to the core , and to reduce occupational radiation exposure.

TRENDS OF WATER CHEMISTRY

Dissolved oxygen and hydrogen

A typical concentration profile of oxygen and hydrogen is shown in Fig. 3 measured in the cases of hydrogen addition and without hydrogen addition chemistry. At the rated reactor power, 15 - 17 Nm³/h of hydrogen injected to the feed water system keeps the oxygen level at the header less than 15 ppb and the ratio of hydrogen to oxygen less than 15. The ratio is kept to ensure the reliability of zircaloy-2 fuel clad (ref. 6). Hydrogen and oxygen concentration levels at the header have been maintained in 140 - 180 ppb for hydrogen and 12 - 15 ppb for oxygen.

Cr-51

In the case of short term - less than a month hydrogen addition, it is often reported that hydrogen addition reduces

soluble Cr-51 concentration level to approximately 1/100 of without hydrogen addition (ref. 1,7). Continuous hydrogen addition from plant lay up, however, reduces Cr-51 concentration only in initial 2 - 3 months of reactor operational cycle as shown in Fig. 4. After half an year of continuous hydrogen addition, soluble Cr-51 concentration increases to $2 - 5 \times 10^{-3} \mu\text{Ci/ml}$ which is the same level as of normal water chemistry. Insoluble Cr-51, which is collected on the 0.4μ filters, changes notably with long term hydrogen addition. After the continuous hydrogen addition started, the change of insoluble Cr-51 resembles to of soluble Cr-51 while the insoluble Cr-51 kept constant in the order of $10^{-5} - 10^{-4} \mu\text{Ci/ml}$ before the commencement of hydrogen addition.

Co-60

Soluble activity concentration in the reactor coolant has been doubled with continuous hydrogen addition as shown in Fig. 5 while insoluble Co-60 has not changed. The buildup of Co-60 on the pipeworks is indicated in Fig. 6. The buildup increased faster after the commencement of hydrogen addition. The buildup rate on replaced new pipes of Type 316L stainless steel is larger than that on Type 304 stainless steel pipes.

Iron levels in condensate and feed water

Oxygen concentration in condensate has been reduced with hydrogen addition from 10 - 20 ppb to less than 1 ppb. The low oxygen concentration causes the increase of soluble iron concentration in condensate as shown in Fig. 7. The insoluble

iron concentration in the feed water increased from 2 - 5 ppb to 10 ppb in a year after the commencement of hydrogen addition test. This change is caused by poor crud removal ability of condensate demineralizers. The rising of insoluble iron concentration in the feed water was suppressed in 1986 with more careful backwash of resins using three times volume of backwash water.

Chemical form change of iron crud

No chemical form change is observed in the iron oxide suspended in the reactor coolant and the oxide deposited on fuel cladding surface as shown in Tables 1 and 2. The increases of fraction and amount of $\alpha\text{-Fe}_2\text{O}_3$ would be caused by the increase of crud concentration in the feed water as previously mentioned.

Electrochemical potential measurement

Electrochemical potential measurement of the Type 304 stainless steel and platinum in the reactor water has been continued since the beginning of the hydrogen addition using two different types of reference electrodes as shown in Fig. 8. The internal type electrode basically gives thermodynamic meaningful value but is sensitive to the hydrogen intrusion into the electrode internals. As the external pressure balanced type electrode is isolated from the hydrogen contained in the high temperature reactor water with the connecting tube which is filled with water and cooled with external coolant, it was used to correct the potential deviation of the internal electrode caused by the hydrogen intrusion. The connecting tube also avoids liquid junction

potential between high temperature reactor water and KCl solution. The reference electrodes have realized steady potential measurement for more than 500 hours without maintenance work as shown in Fig. 9. The electrochemical potential of Type 304 stainless steel is -210 mV(SHE) with the hydrogen addition water chemistry (ref. 8).

MATERIAL INTEGRITY

In-plant and laboratory tests have been continued to confirm the material integrity in long term hydrogen addition water chemistry. Bolt-WOL, compact tension (CT), slow strain rate test (SSRT), and uniaxial constant load test (UCLT) for Type 304 stainless steel are under way. The UCLTs for Zr-2.5%Nb is also implemented. And hydrogen uptake by the zircaloy-2 is measured in a laboratory test.

Bolt-WOL and CT examinations

To evaluate the crack growth rate of Type 304 stainless steel, six bolt-WOL specimens and three CT coupons are set in the in-plant test facilities to which the reactor water flows from the header. All test specimens are sensitized as follows : 1050°C for 30 min, 750 °C for 100 min, and 500 °C for 24 hours. The stress intensity factors are set at 70, 100, and 150 kg/mm^{3/2} for every two bolt-WOL specimens and 80, 130, and 190 kg/mm^{3/2} for each CT specimen since the critical stress intensity factor K_{Ith} at the low oxygen concentration would be greater than 50 - 70 kg/mm^{3/2}

reported as K_{Ith} at higher oxygen concentration region, in the order of 1 ppm (ref. 9). No crack growth is observed on the specimens after 7000 hours of bolt-WOL test and 2000 hours of the CT test.

SSRTs

The SSRTs were carried out in four cases using six Type 304 and six Type 316L stainless steel specimens in continuous hydrogen addition water chemistry. The results are listed in Table 3. No IGSCC was observed on the fractured surface of all the specimens.

UCLTs

Seven types of 38 specimens as shown in Table 4 have been immersed in the autoclave of the in-plant test facilities for over 7000 hours. No specimen has broken.

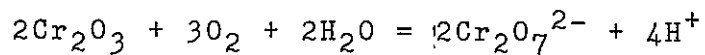
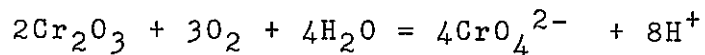
Hydrogen uptake by zircaloy-2

Hydrogen uptake by zircaloy-2 has been measured in two laboratory autoclaves to confirm the integrity of fuel clad. Dissolved oxygen concentration in an autoclave is kept 200 ppb to simulate the hydrogen not added water chemistry and in the other autoclave oxygen and hydrogen are kept 20 ppb and 1000 ppb, respectively correspond to the hydrogen addition water chemistry. Electric conductivity of the water in the autoclaves is maintained lower than 0.45 $\mu\text{S}/\text{cm}$, and pH is kept 6.3 - 6.9. The hydrogen uptake measured during in 13000 hours is shown in Fig. 10. Only small difference is observed in the two cases.

DISCUSSION

Trends of Cr-51

The equilibrium reactions



occur in reactor water and on pipe inner surface in relation to the oxygen concentration of the environment. The low oxygen concentration due to hydrogen addition suppresses sexivalent chromium dissolution during a few months of plant operation. The accumulated Cr_2O_3 on the pipe surface is gradually released to the reactor water and the soluble chromium would increase to keep equilibrium relation.

Co-60

The activity buildup shown in Fig. 6 possibly corresponds with the increase of Co-60 concentration in the reactor water with continuous hydrogen addition as indicated in Fig. 5. The increase of Co-60 concentration in reactor water would be caused by acceleration of Co-60 dissolution from deposited iron oxide on fuel clad which contains irradiated cobalt. The hydrogen addition would slightly change the oxide form from hematite to magnetite and accelerate the cobalt dissolution because the solubility of

magnetite is larger than hematite. The chemical form change of iron oxide, however, was not observed since the accumulated amounts of Co-60 and iron on the fuel surface is extremely larger than those which occurs the concentration change in the reactor water.

The increase of Co-60 concentration in the reactor water means shortening of cobalt residence time on the fuel surface. Longer observation for the Co-60 concentration should be necessary since the shortening of cobalt residence time on fuel surface causes a reduction of specific activity of the cobalt in the reactor water for longer time plant operation.

The replaced Type 316L stainless steel pipes indicate faster Co-60 buildup than old Type 304 stainless steel pipes. The fact is consistent with the results of others (ref. 10,11).

Oxygen concentration in condensate

The oxygen content reduction in the main steam with hydrogen addition decreases the oxygen and increases the soluble iron concentration in the condensate as shown in Fig. 7. The amount of oxygen introduced to the condensers with main steam is reduced from 5 Nm³/h to 0.6 Nm³/h by the hydrogen addition.

Electrochemical potential

A long term, longer than 500 hours, stable measurement was established on electrochemical potential after improvements of maintenance procedure for electrodes. The reference electrodes

were troubled with consumption of AgCl with hydrogen and dilution of electrolyte with water penetration to the internals. And the sample electrodes requires strict electric insulation with the autoclave. Careful insulation check for the sample electrodes and calibration for the reference electrode at a room temperature should be carried out.

CONCLUSION

Two years' continuous hydrogen addition and material tests give the following results.

-The hydrogen addition increased the Co-60 concentration in the reactor coolant and accelerated Co-60 buildup on the pipe surface.

-No symptom of IGSCC growth on Type 304 stainless steel is observed in CT, bolt-WOL, SSRT, and ULCT.

-No acceleration is observed on the hydrogen uptake rate by zircaloy-2 in hydrogen added water chemistry.

ACKNOWLEDGEMENT

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REFERENCE

1. NIIZAWA T., KITABATA T., "Effect of Hydrogen Addition on Stress Corrosion Cracking in the Fugen Nuclear Power Station", Proc. of 4th Int. Conf. on Water Chemistry of Nuclear Reactor Systems, Bournemouth, Vol.2, Paper 17, BNES, (1987).
2. COWAN R. L. , INDIG M. E. , KASS J. N. , LAW R. J., and SUNDBERG L. L., "Experience with Hydrogen Water Chemistry in Boiling Water Reactors", Proc. of 4th Int. Conf. on Water Chemistry of Nuclear Reactor Systems, Bournemouth, Vol.1, Paper 13, BNES, (1986).
3. HALLDEN E., and ROTH T., "A Reactor Test for the Demonstration of Crack Arrest during Water Chemistry in BWR Forsmark-1", *ibid.*, Paper 16, BNES, (1986).
4. BILANIN W., CUBICCIOTTI D., JONES R. L., MACHIELS A. J., NELSON L., and WOOD C. J., "Hydrogen Water Chemistry for BWRs", *Progress in Nuclear Energy*, 20, No. 1, 1-12 (1987).
5. AKEBI M., and FUJIKI I., "Development of Plutonium Fuel Utilization in Fugen Type HWR", Int. Conf. on Nuclear Power Experience, Vienna, Sept. 1982, IAEA, IAEA-CN-42/295, (1982).
6. COX B., "Effect of Hydrogen Injection on Hydrogen Uptake by BWR Fuel Cladding", EPRI NP-3146, Final Report, (1983).
7. "Materials Behavior in Hydrogen Water Chemistry in the Ringhals-1 BWR", EPRI NP-3992M Final Report, (1985).
8. UEDA S., and IWAI M., "Corrosion Potential Measurement in Hydrogen Water Chemistry of the Fugen Nuclear Power Station" Proc. of 1987 Fall Meeting of Atomic Energy Society of Japan Vol. 2, 194

(1987).

9. SCHMIDT C.G., CALIGIURI R. D., and EISELSTEIN E., "Intergranular Stress Corrosion Cracking of Low Temperature Sensitized Type 304 Stainless Steel Pipe Welds", Proc. of the Int. Symposium on Environmental Degradation of Materials in Nuclear Power Systems - Water Reactors, 423 - 437 (1983).

10. LIN C. C., SMITH F. R., RUIZ C. P., KOBAYASHI N., INAMI I., IGARASHI N., URUMA Y., OCKEN H., and WOOD C. J., "Cobalt Deposition Studies in GE Vallecitos Test Loops", Proc. of 4th Int. Conf. on Water Chemistry of Nuclear Reactor Systems, Bournemouth, Vol.1, Paper 43, BNES, (1986).

11. MARBLE W.J., COWAN R.L., and WOOD C. J., "Control of Cobalt-60 Deposition in BWRs", Proc. of 4th Int. Conf. on Water Chemistry of Nuclear Reactor Systems, Bournemouth, Vol.1, Paper 42, BNES, (1986).

Table 1 $\alpha\text{-Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$ ratio of iron crud suspended in reactor water

	Before H ₂ addition	After H ₂ addition
$\alpha\text{-Fe}_2\text{O}_3$	80 ~ 70 %	85 ~ 70 %
Fe_3O_4	20 ~ 30 %	15 ~ 30 %

Table 2 Chemical form of crud deposited on fuel surface

		Experienced without H ₂	H ₂ addition experienced
Fuel history	Exposure time	1979. 4 - 1984. 2	1983. 1 - 1986. 7
	EFPD	806	880
	Fuel exposure	12. 7 GWd/t	16. 0 GWd/t
Chemical analysis	Crud deposition	7. 5 mg/cm ²	10 mg/cm ²
	Fe/Ni/Cr ratio	97. 3 : 1. 5 : <0. 1 (%)	98. 0 : 1. 1 : <0. 1 (%)
	Crud formula	almost $\alpha\text{-Fe}_2\text{O}_3$	almost $\alpha\text{-Fe}_2\text{O}_3$
	Co-60 activity	100 - 370 $\mu\text{Ci}/\text{cm}^2$	130 - 440 $\mu\text{Ci}/\text{cm}^2$
	Co-60/total Co	20 - 26 $\mu\text{Ci}/\mu\text{g}$	18 - 23 $\mu\text{Ci}/\mu\text{g}$

Table 3 Results of SSRTs .

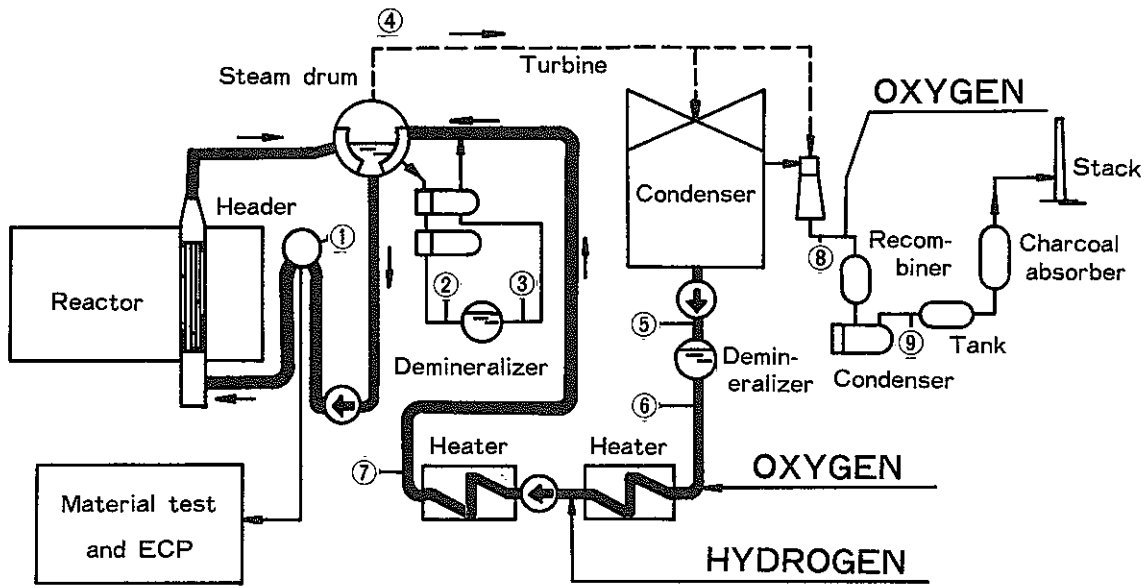
Test No ¹⁾	Material ²⁾	Carbon content (%)	Dissolved O ₂ (ppb) ³⁾	results
1	304 SS	0.06	8 - 9	No IGSCC
2	304 SS	0.06	9	No IGSCC
3	316L SS	0.011	10 - 11	No IGSCC
4	316L SS	0.011	10 - 11	No IGSCC

NOTES:

- 1) Three SSRT specimens are examined for each test.
- 2) All specimens are sensitized at 1050 °C for 30 min, 750 °C for 100min, and 500 °C for 24 hours.
- 3) The oxygen concentration indicated in this table is the values measured at the outlet of the autoclave. The inlet oxygen concentration is maintained at 12 - 15 ppb.

Table 4 Conditions for UCLTs

Material	Heat treatment	Stress intensity (kg/mm ²)	Number of specimens
HT Zr-2.5% Nb (pressure tube)	With oxide film formed in autoclave	39	12
Inconel weld part between Type 403M and Type 304	Fabricated from weld part		
	as weld	20	4
	500 °C × 24hrs	20	4
	Fabricated from Type 430M		
	moderate heat treatment	30	3
	moderate heat treatment	30	3
	+cold fabrication		
Type 304 SS	Weld part + 500 °C × 24hrs	20	6
	Weld part + 500 °C × 24hrs	30	6



Sampling portion

- | | |
|---------------------|-------------------------------------|
| ① : Header | ⑤ : Condensate demineralizer inlet |
| ② : Clean up inlet | ⑥ : Condensate demineralizer outlet |
| ③ : Clean up outlet | ⑦ : Feed water |
| ④ : Main steam | ⑧ : Recombiner inlet |
| | ⑨ : Recombiner outlet |

Fig. 1 Schematic diagram of primary cooling system

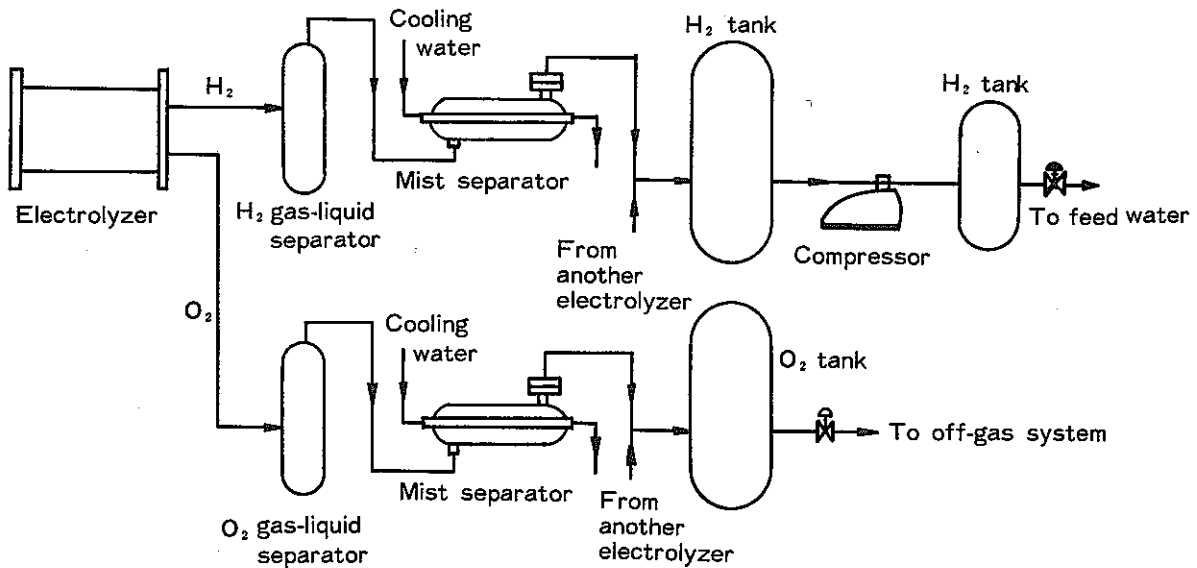


Fig. 2 Schematic diagram of hydrogen and oxygen generation system

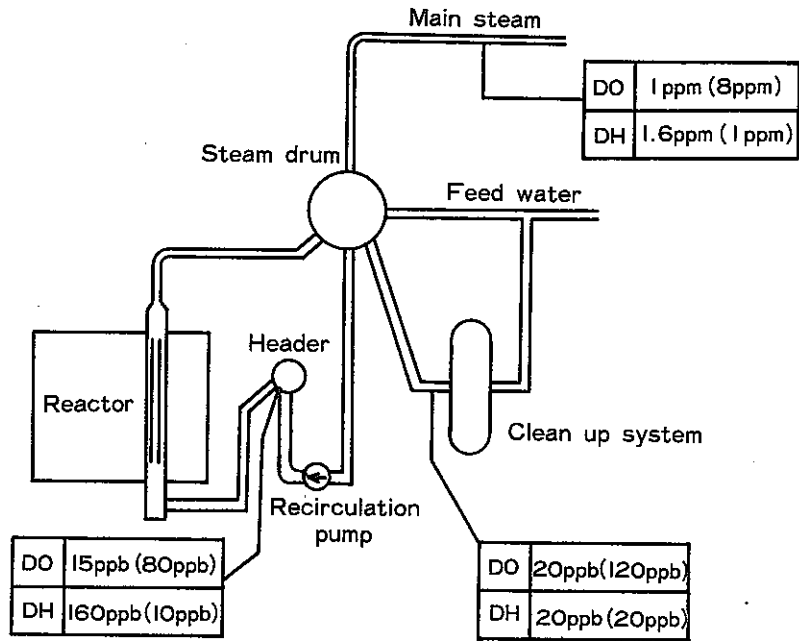


Fig. 3 Dissolved oxygen and hydrogen concentration profile with hydrogen addition

Note: The values in parenthesis mean concentration measured without hydrogen addition.

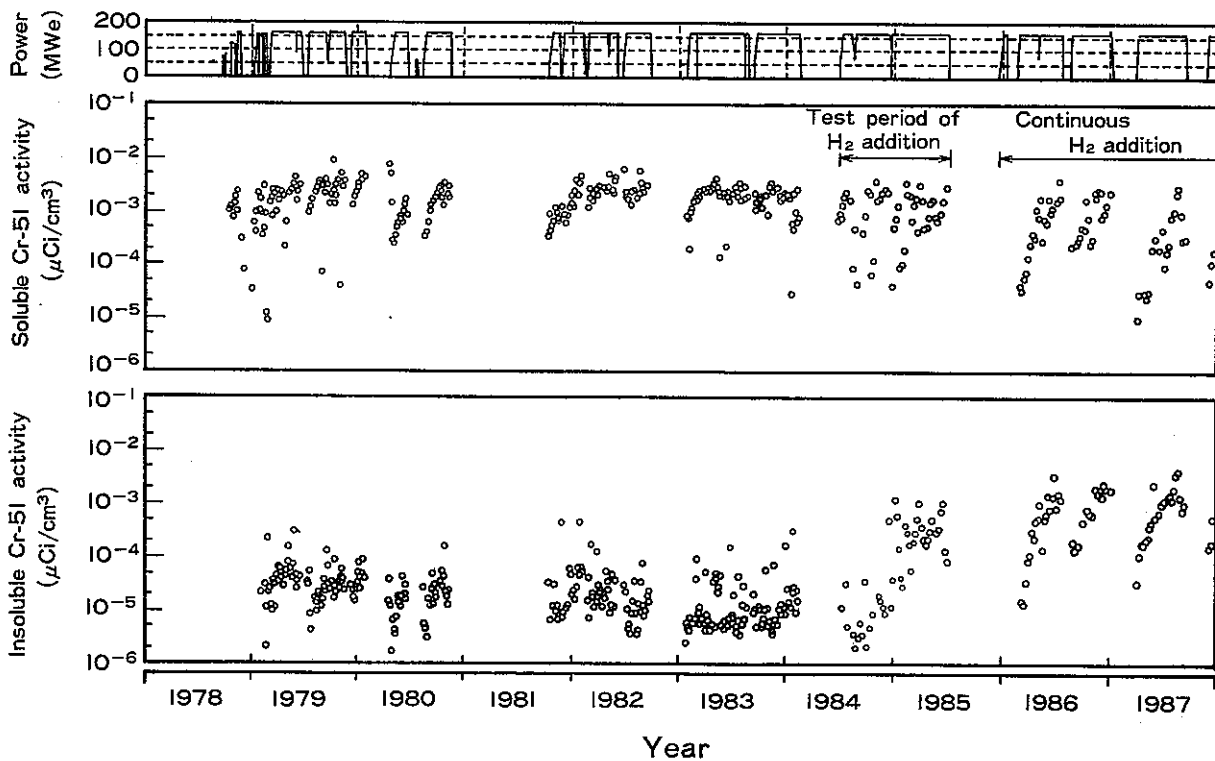


Fig. 4 Change of Cr-51 concentration in reactor coolant with hydrogen addition

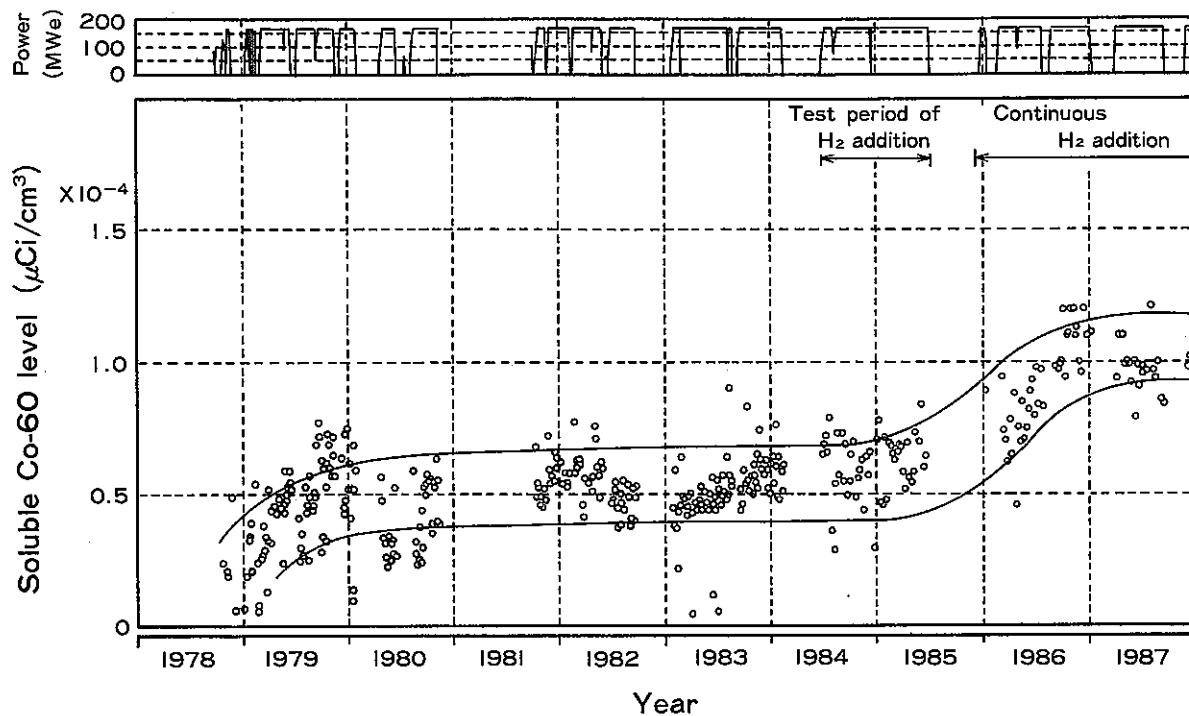


Fig. 5 Change of Co-60 concentration in primary coolant with hydrogen addition

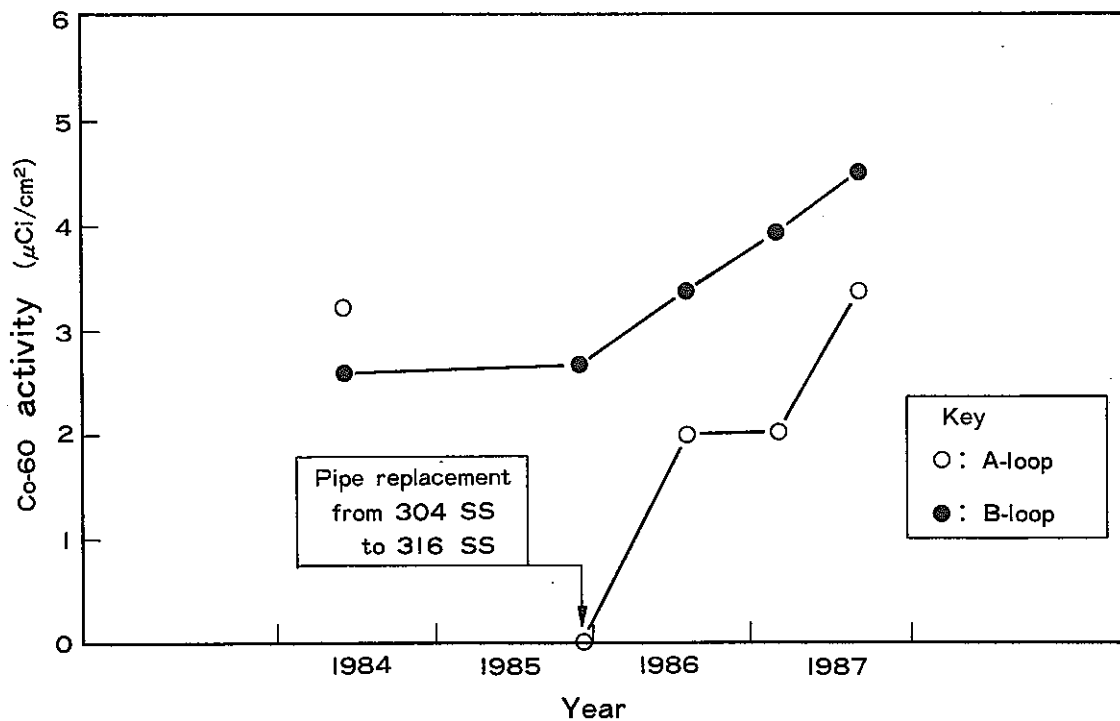


Fig. 6 Co-60 buildup at recirculation pump outlet

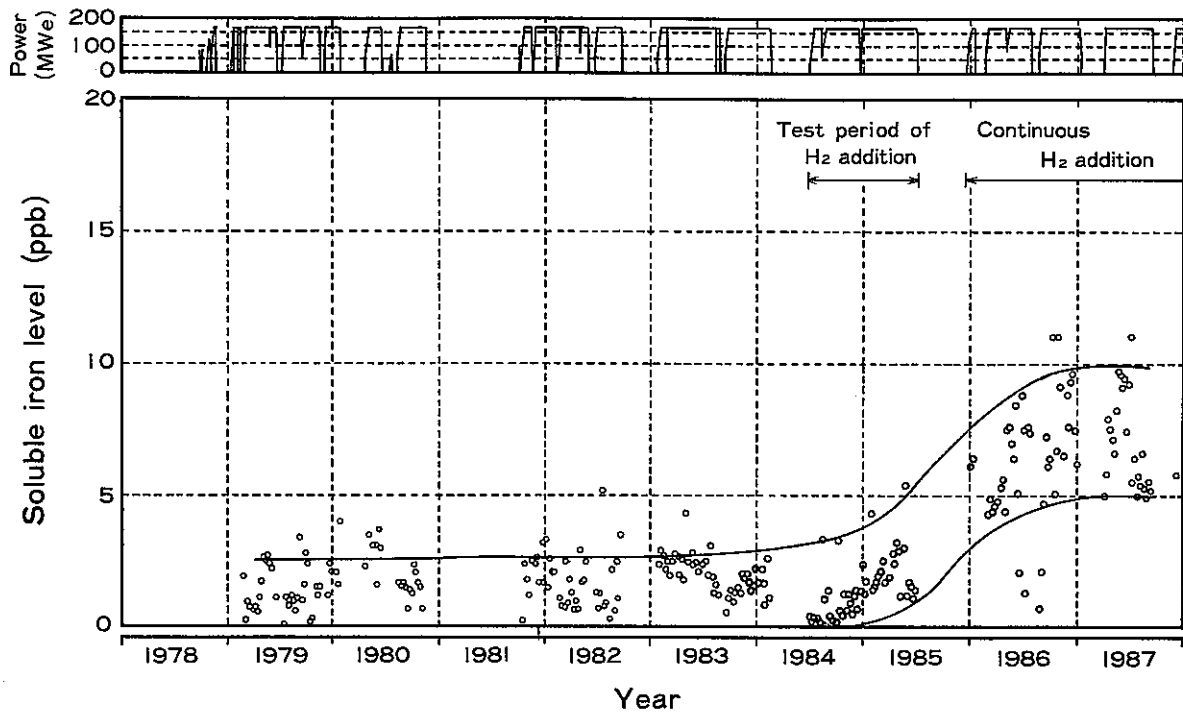


Fig. 7 Change of soluble iron concentration in condensate

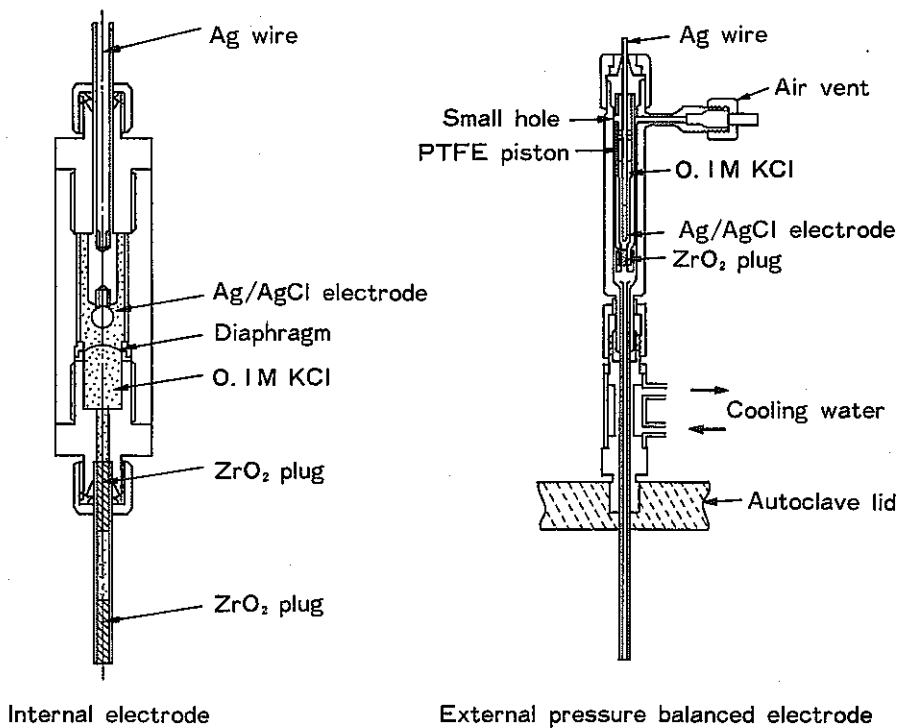


Fig. 8 Two reference electrode assemblies

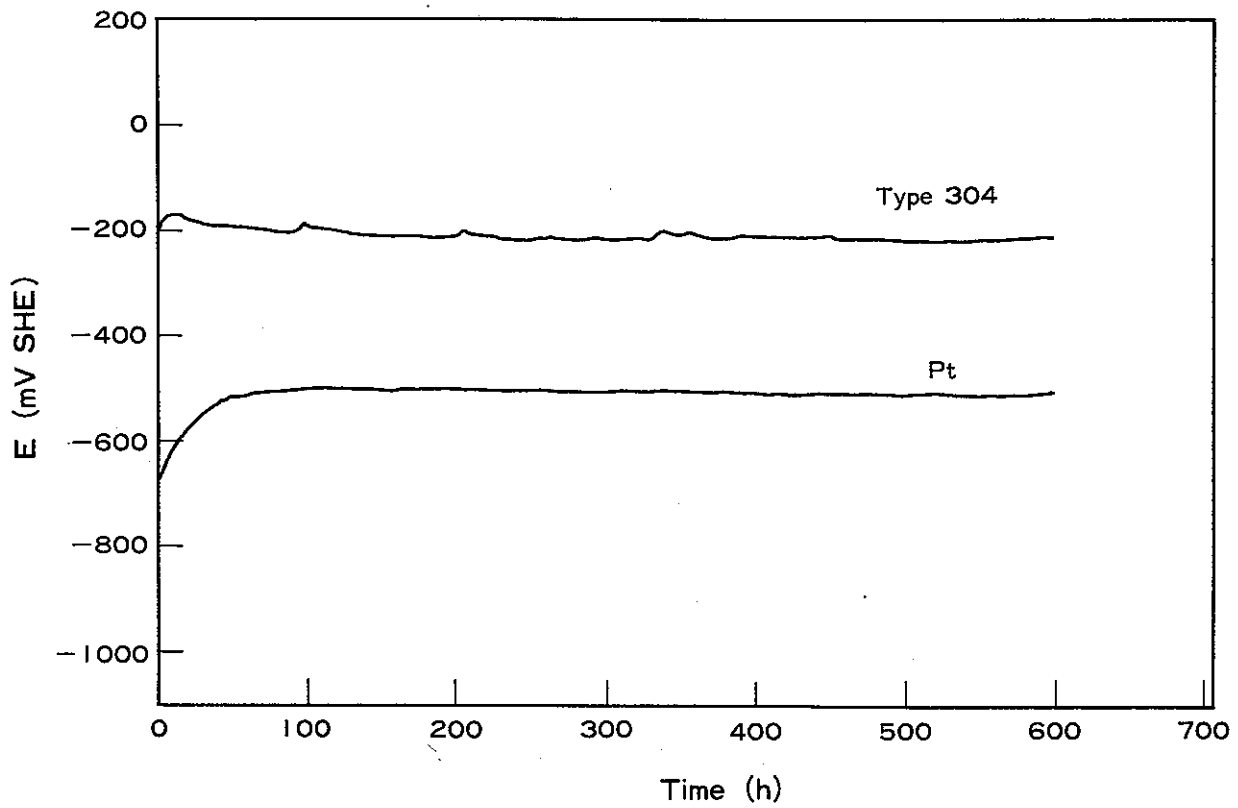


Fig. 9 Electrochemical potential of Type 304 stainless steel and platinum measured in hydrogen added water chemistry

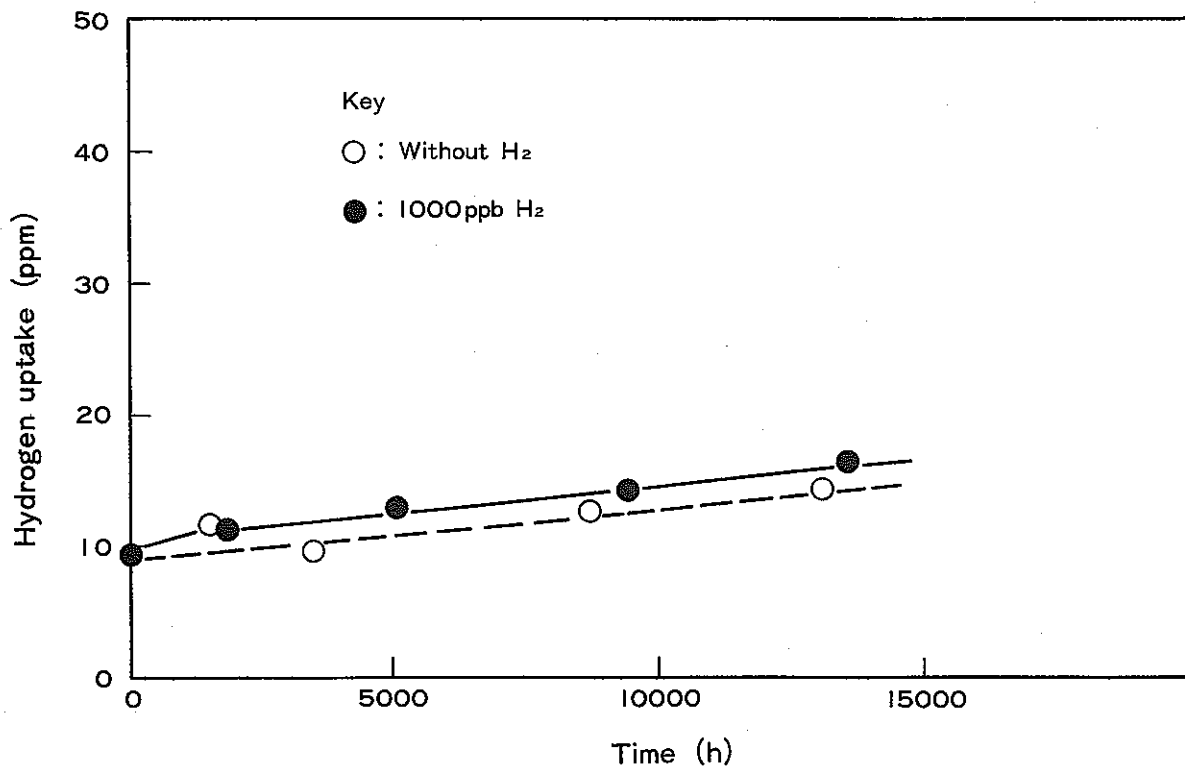


Fig. 10 Hydrogen uptake of zircaloy-2