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EXPERIENCE OF WATER CHEMISTRY IN FUGEN HWR

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Experience of the heavy water and primary coolant chemistry of the Fugen is described. Deterioration has been observed in the weak basic ion exchange resins used in the heavy water purification system. Extensive studies to prolong the life of resins are now going on. Amount of iron in the feed water has been reduced by means of oxygen injection, operational improvement of condensate demineralizers, hot drain-off of the feed water circuit, and sufficient flushing prior to operations.

INTRODUCTION

1. The 165 MW(e) prototype HWR Fugen came into commercial operation in March 1979 after one year of commissioning and has operated for over 900 EFPD (ref. 1)(ref. 2)(ref. 3)(ref. 4)(ref. 5). The reactor has generated more than three million MWh and has achieved an average load factor of 53% for past four years. The plant performance and reactor characteristics have been demonstrated to be satisfactory during a series of the start-up tests and the four years' operation. No fuel failure has been experienced. Stress corrosion cracking was found in Type 304 stainless steel pipes of the residual heat-removal system and emergency core-cooling system during the scheduled shutdown in November 1980. These Type 304 stainless steel pipes have been replaced with Type 316 (low carbon) stainless steel.

DESCRIPTION OF THE PLANT

2. The Fugen is a direct-cycle, boiling light water cooled, heavy water moderated, pressure tube type reactor using uranium-plutonium mixed oxide fuel. Reactivity is controlled by the control rods and the adjustment of boron-10 concentration in the moderator. The main design data are listed in Table 1. The reactor has two independent primary coolant circuits, each consisting of a steam drum (carbon steel internally lined with stainless steel), two recirculation pumps and associated pipes (mainly Type 304 stainless steel). Each of 224 cluster type fuel assemblies is loaded in a vertical Zr-2.5%Nb alloy pressure tube. Condensate feed water system consists of three condensate pumps, four demineralizers, five feed water heaters, and three feed water pumps, of which two pumps are capable of supplying 910 t/h of water at the rated power. Carbon steel is mainly used in pipings of this system. A diagram of the primary coolant and feed water purification system is shown in Fig. 1.

3. The primary coolant purification is achieved by the use of two mixed ion exchange beds, each consisting of 1.35 m^3 mixed resins (2:1 cation and anion) and being capable of treating up to 60 t/h from the 60 t primary coolant inventory. Under full power opeation the resin beds are operated at 30 ∿ 40°C. The condensate demineralizers consist of four mixed ion exchange beds with 3.3 m^3 mixed resins (2:1 cation and anion). They are operated at 30 ∿ 40°C and treated with full flow of the condensate.

4. A diagram of the moderator and helium gas flow circuit is shown in Fig. 2. The moderator system consists of heavy water cooling circuit and purification system, and is made of stainless steel and zircaloy-2 (calandria tube). The heavy water cooling circuit keeps the temperature about 49°C at the outlet of the heat exchangers. The heavy water purification system has two purification resin beds which consist of 0.5 m^3 of strong acidic cation resins and 0.5 m^3 of weak basic resins to remove impurities except boric acid, and has two poison removal resin beds containing 0.8 m^3 of strong basic resins. This system is capable of treating up to 22 t/h from the 150 t heavy water inventory.

HEAVY WATER CHEMISTRY

Purification of heavy water

5. Heavy water of the Fugen contains no chemical additives except boron. Purification of heavy water is achieved by the use of resin beds in order to prevent corrosion of the materials of the heavy water circuits and to minimize the accumulation of deuterium in the blanket gas. The pH is controlled within 4.5 ∿ 8.5 and the concentration of Cl^- is kept under 0.1 ppm. The B-10 concentration is between 5 ∿ 7 ppm at the beginning of each fuel cycle and radionuclides measured are Co-60 at 10 μCi/l, Co-58 at 0.1 μCi/l, Cr-51 at 5 μCi/l, and H-3 at 2 Ci/l at 800 EFPD. The conductivity has

been kept under 5 μS/cm since October 1978, but it exceeded 7 μS/cm in early days of reactor operation, although the resin bed had designed to keep it under 1.5 μS/cm.

6. The increase of the conductivity is caused by NO_3^- formation in the heavy water. It is considered that the NO_3^- is generated by fixation of gaseous N_2 which is considered in the helium blanket and by radiolysis of the impurities released from the resins. Gaseous N_2 is contained in the helium less than 0.2 vol% after an annual maintenance of the helium system, and it is reduced slowly during the reactor operation. But the amount of N_2 consumed is not enough to form the total amount of the NO_3^-. The weak basic resins used in the heavy water purification system contain diethylenetriamine as active groups. Amines, imines, oximes and unidentified organic components are released from the resins when they are oxidized. These organic components are detected by the experiment using light water containing hydrogen peroxide.

7. These facts suggested a mechanism of the conductivity increase. Deuterium peroxide being present as a product of radiolysis of heavy water oxidizes the weak basic resin and decomposes it into organic components including nitrogen atoms. The components are decomposed by radiolysis in the core and form NO_3^-, CO_3^{--} and so on. These electrolytes cause the increase of conductivity of the heavy water.

8. Intermittent service of the purifier was therefore employed in order to suppress the degradation of resins since September 1978. As a result of this improvement, the conductivity of the heavy water has been maintained under the specification limit of 5 μS/cm for four years.

Prolongation of in-service period of purification resin beds

9. Resins used in the moderator purification system are supplied in the forms of H^+ and OH^-. To avoid downgrading of the D_2O by H_2O, it is necessary to remove all light water from the resin interstice, and to convert the active groups D^+ and OD^- forms before the installation of the resins. Approximately 2 m^3 of pure heavy water is required to deuterize the resins installed in a purification resin bed.

10. Since prolongation of in-service periods of the resins was necessary to reduce the amount of the heavy water used for the deuterization, following methods were examined.

(a) decomposition of deuterium peroxide by catalyzers

(b) application of strong basic resin

(c) lowering the temperature of the purification resin bed

(d) use of well regenerated resins.

11. Decomposition of deuterium peroxide by catalyzers
Deuterium peroxide in the heavy water oxidizes resins in the purification system. According to the experiment using hydrogen peroxide, it was found that in-service period of resins was approximately doubled when the resins were used in the water free from hydrogen peroxide.

12. Thereupon, installation of a catalyzer column in the upsteam of the purification resin bed was planned. For this column, a Pt plated catalyzer on a stainless steel mesh and a Pt-balck catalyzer on sintered ceramics were selected, since they have high efficiency to decompose hydrogen peroxide. These catalyzers were examined on their durability by experiments using a model column connected to the heavy water circuit of the Fugen. The results obtained in these experiments were that the Pt plated catalyzer degraded at the early stage of its service, but the Pt-black catalyzer was able to use more than 2000 hours as shown in Fig. 3.

13. Application of strong basic resins In order to reduce the damages of resins by deuterium peroxide, application of strong basic resins saturated with boron was examined. The oxidation of resins was observed by the experiments in which the resins were exposed in light water containing hydrogen peroxide and the variation of their exchange capacity was measured. It was found that strong acidic cation resins were most stable against hydrogen peroxide and strong basic resins had higher stability than weak basic anion resins. At the same time it was confirmed that the equilibrium amount of boron adsorbed on strong anion resins depended considerably on the boric acid concentration and temperature.

14. Lowering the temperature of the purification resin bed Ion exchange capacity of the heavy water purfication bed is increased and decomposition rate of the resins due to deuterium peroxide is decreased by the reduction of the heavy water temperature. This effect was confirmed experimentally. Light water containing same impurities as that of the heavy water was passed through 10 ml of the resins, and the conductivity of the effluent was measured continuously. It was found that, as shown in Fig. 4, the life of the resins was prolonged three times longer by lowering the temperature from 49°C to 25°C, where the conductivity at the break point was defined as 3 μS/cm.

15. Use of well regenerated resins The commercially available weak basic resin contains 0.5 ∿ 2.0% of residual chloride ion because of poor regeneration level by manufacturers. There are usually nitrate and carbonate ion in the heavy water generated from the resins or dissolved nitrogen by radiation. As the adsorption constant of the nitrate ions to the weak basic resins is higher than that of chloride ions, the chloride ions are replaced by the nitrate ions while the heavy water is treated in the column. The chloride concentration and the conductivity, therefore, increase as shown in Fig. 5. Longer term service of the resins is expected by the reduction

of the residual ions which cause the rapid increase of the conductivity in the effluent.

16. A test column with well regenerated resins was connected to the heavy water system, and conductivity and concentration of the chloride ion were measured. It was confirmed that the rapid increase was not found for the well regenerated resins. Regeneration level of 250 g-NaOH/l-resins was employed since 1982 as a result of the experiment. It is considered that a small peak found at 80 hours on the conductivity curve in Fig. 5 is due to the break through of carbonate ion which has very low affinity to the weak basic resins.

Selection of methods for prolongation of the in-service periods of resins

17. Among above-mentioned methods, the decomposition of deuterium peroxide was not applied to the plant because of the following reasons.

(a) Used catalyzers increase radioactive wastes.

(b) Exchanging of catalyzers is difficult to handle since the Pt-black catalyzers are fragile, and the radiation dose of the catalyzer surface is too high.

(c) The method of lowering of the temperature of the purification resin bed is more effective than the usage of catalyzers.

Although the application of strong basic resins was promissing in the prolongation of in-service periods of purification resin beds, it was not applied to the system since the modifications of the heavy water system were needed. The method of lowering the temperature of the purification system is considered to be most effective. To carry out this method, the following subjects were examined and settled:

(a) control of the moderator temperature which affects the core reactivity

(b) optimum temperature of the heavy water through the purification resin bed and the feasibility of the installation of the cooler

The well regenerated resins have been used since the beginning of 1983.

WATER CHEMISTRY OF PRIMARY COOLANT

18. The coolant water in Fugen is kept neutral with no chemical additives as in BWRs'. Specifications of primary coolant is shown in Table 3, and the observed results show the good chemistry. Gamma spectroscopic measurements are made twice a week and major nuclides found are Co-60 at ∿ 0.05 μCi/l, Co-58 at ∿ 0.07 μCi/l, Mn-54 at ∿ 0.02 μCi/l and I-131 at ∿ 0.002 μCi/l.

19. One of philosophies of the controlling the primary coolant is to suppress iron input to the primary coolant as low as possible, since the reduction of iron input is effective to reduce surface dose rate of the primary circuits, as often reported (ref. 6). From this point of view, it is employed to inject oxygen into the feed water and to improve the operation of the condensate demineralizers. Also during outage for maintenance of the station, hot drain-off and clean-up of the feed water circuit are performed.

20. Oxygen injection It is important to form a thin layer of iron oxide on the surface of the pipes to reduce dissolution of iron, as carbon steel is used in the feed water circuits except for the feed water heater tubes. Gaseous oxygen has been injected into the condensate at the outlet of the demineralizers, and the concentration of dissolved oxygen is maintained between 20 and 60 ppb at the outlet of the fifth

heater. Behaviour of iron concentration which observed in the experimental injection is shown in Fig. 6. It was found that the ionic iron at the fifth heater decreased significantly from 10 ppb to 1 ppb. Oxygen has been injected continuously, thereafter, to keep ionic iron concentration less than 1 ppb in the feed water.

21. The radiation dose rate at the outlet of a reactor recirculation pump is shown in Fig. 7. It is clear that the oxygen injection gave a remarakable reduction in the build-up tendency of the dose rate.

22. Operational improvements of condensate demineralizers
The concentration of soluble iron has been kept as low as 0.1 ppb by the oxygen injection into the condensate, but that of insoluble iron was 10 ppb in 1978. Several experiments were carried out so as to understand the mechanisms of crud removal by resin beads. The crud iron concentration in the condensate at the inlet and outlet of each demineralizer was measured for a month. The filtration efficiency of the demineralizer dropped rapidly in a few days of service and gradually recovered for following four weeks. This characteristics of the crud removal by resins showed a tea spoon-like curve as shown in Fig. 8. The crud distribution in the demineralizer was measured using a model column made of translucent plastic. The plastic column had an inner diameter of 1 cm and a height of 1.3 m and was connected to the condensate system. A scanning electron microscope was used for this experiment. Most of crud was dendritic and amorphous, and trapped in a shallow part of the column from the upper surface to 30 cm in depth. On the other hand, very fine crud (less than 1 μm in diameter) was distributed throughout the column.

23. These results have led to the following conclusions regarding the filtration mechanism.

(a) At the early stage of service of the demineralizer, very fine crud is adsorbed by electrostatic force caused by zeta potential (ref. 7) and makes thin layer on the resin surface which causes rapid drop of the filtration efficiency.

(b) After this stage, choking of the resin interstice occurs and a cake layer is formed at the shallow part of the demineralizer by the crud itself. The cake layer makes a recovery of the filtration efficiency.

24. The service period of the condensate demineralizers has been altered from two weeks to four weeks since 1981 to make use of the high crud removal efficiency at the "handle part" of the tea spoon-like curve. All of four demineralizers are served instead of three units to lessen the rate of pressure drop increase due to four weeks' usage. The resins are backwashed completely using 60 m^3 of water for regeneration of each demineralizer since the crud catched in resins is increased by the prolongation of in-service period.

25. As a result of these improvements, the crud iron concentration at the outlet of the condensate demineralizers has been successfully reduced from 5 ppb to 1 $\sim$ 2 ppb against 30 ppb at the inlet.

<u>Chemistry control during outage</u>

26. Input of iron into the primary coolant circuits has been reduced by oxygen injection and operational improvement of the condensate demineralizers as described previously, but crud formed in the condensate and the feed water circuits during a long term outage are easily carried into the primary system at the start up period. Hot drain-off and clean-up operation are employed as the countermeasures against crud formation problem during the outage for maintenance.

27. Hot drain-off Hot drain-off technique has been employed in order to prevent the generation of rust on steel surface since 1981. Feed water pipings are heated up to 60°C by the recirculation of the condensate through the clean-up line for two or three days after the shut-down of the reactor. Then, the hot water is drained off and the manholes on the condenser and turbine are opened. The surface of the condenser and pipes are completely dried by residual heat of the components. By the hot drain-off, the clean-up time was reduced to ten days which is half as much as the previous time.

28. Clean-up operation The clean-up operation of the feed water line is performed by using feed water recirculation line (e.g. condensate recirculation line, feed water pumps minimum flow line, feed water clean-up line) before the start-up of reactor at a flow rate of 250 m^3/h. The crud is removed in the condensate demineralizers or drained from the hot-well of the condenser. Iron input to the primary coolant circuit at the start-up of the reactor after a long outage is suppressed to a very low value of 110 g/day which is nearly equal to that of normal operation.

CONCLUSIONS

29. Purities of the heavy water and the primary coolant of the Fugen are controlled within the specification limit. This proves the validity of the water chemistry in the Fugen. To prolong the in-service periods of the heavy water purifier, the well regenerated resins have been used and lowering the temperature of the purification resin bed has been planned. In order to reduce the dose rate build-up, suppression of iron input into the primary coolant has been achieved by oxygen injection into the feed water, improvement of regeneration method of the condensate demineralizer, hot drain-off, and clean-up operation of the feed water circuit. The dose rate of the surface of the primary coolant circuits has been suppressed sufficiently.

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Table 1 Station design data

REACTOR TYPE	
Heavy water moderated, boiling light water cooled, pressure tube type	
OUTPUT	
Gross thermal output ...	557MWt
Gross electrical output	165MWe
CORE	
Core height	3700 mm
Core diameter	4050 mm
Lattice	240 mm square lattice
Number of fuel channels	224
Fuel inventory	34 t as metal
FUEL	
Fuel material	MOX type A (%Puf) 0.8/0.8/0.6 MOX type B (%Puf) 1.6/1.6/1.1 UO_2 type A (% ^{235}U) 1.5/1.5/1.5 UO_2 type B (% ^{235}U) 1.9/1.9/1.9
Pellet diameter	14.4 mm
Fuel assembly	28 fuel rods, 12 spacers
Total length of fuel assembly	4388 mm
Cladding material	Zircaloy-2
Cladding thickness	0.8 mm
PRESSURE TUBE	
Material	Zr-2.5w%Nb alloy
Inside diameter	117.8 mm
Thickness	4.3 mm
Length	5 m
STEAM DRUM	
Diameter	2 m
Length	16 m
Material	Low carbon steel clad with stainless steel
CALANDRIA TUBE	
Material	Zircaloy-2
Inside diameter	156.4 mm
Thickness	1.9 mm
MODERATOR	
Heavy water inventory ..	150 t
Heavy water temperature (max.)	70°C
CONTROL RODS	
Number of control rods .	49
Material	B_4C in stainless steel
Mechanism	Motor-driven wire drum
PRIMARY COOLANT SYSTEM	
Coolant	H_2O
Coolant inventory	60 t
Coolant pressure in steam drum	68 kg/cm^2
Coolant temperature in steam drum	284°C
Coolant flow rate	7600 t/h
Steam exit quality (mean)	14 %
Number of cooling loops	2
PRIMARY CONTAINMENT	
Configuration	Cylindrical
Diameter	36 m
Height	64 m
TURBINE SYSTEM	
Steam pressure	63.5 kg/cm^2
Steam temperature	279°C
Steam flow rate to turbine	910 t/h
Speed	3600 rev/min
Generator rating	200 MVA

Table 2 Chemistry parameters of heavy water

	Unit	Measured value*	Specification
pH	-	5.40	4.5 ∿ 8.5
Conductivity	μS/cm	4.30	< 5.0
Cl^-	ppm	0.03	< 1.0
NO_2^-	ppm	0.06	-
NO_3^-	ppm	1.64	-
SO_4^{--}	ppm	0.02	-

* sampled at the inlet of the purification resin bed

Table 3 Chemistry parameters of primary coolant

	Unit	Measured value*	Specification
pH	-	6.70	5.5 ∿ 8.5
Conductivity	μS/cm	0.15	< 1.0
Cl^-	ppm	< 0.001	< 0.2
SiO_2	ppm	0.06	< 2.0
BO_3	ppm	< 0.005	< 2.0
Dissolved oxygen	ppm	0.15	< 0.4
I-131	μCi/g	1.4 x 10^{-6}	< 0.8

* sampled at the inlet of the clean up purification resin bed

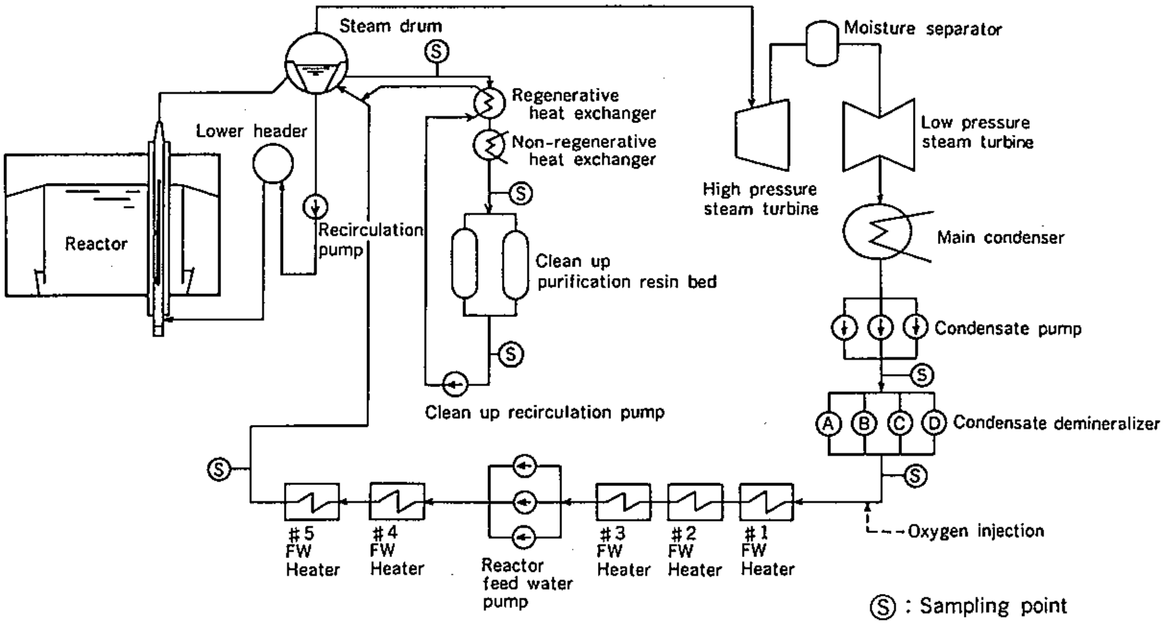

Fig. 1. Schematic diagram of primary coolant and feed water system

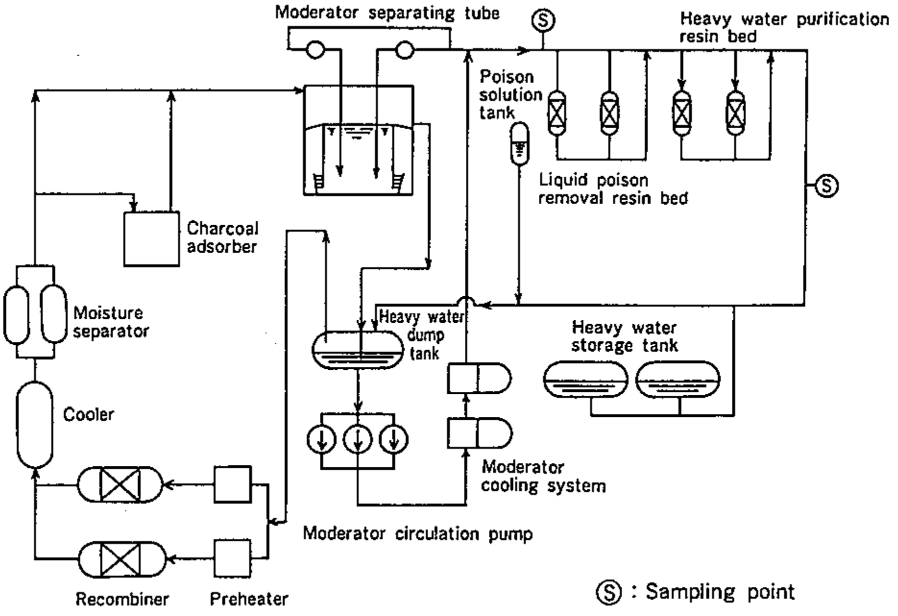

Fig. 2. Schematic diagram of heavy water and helium system

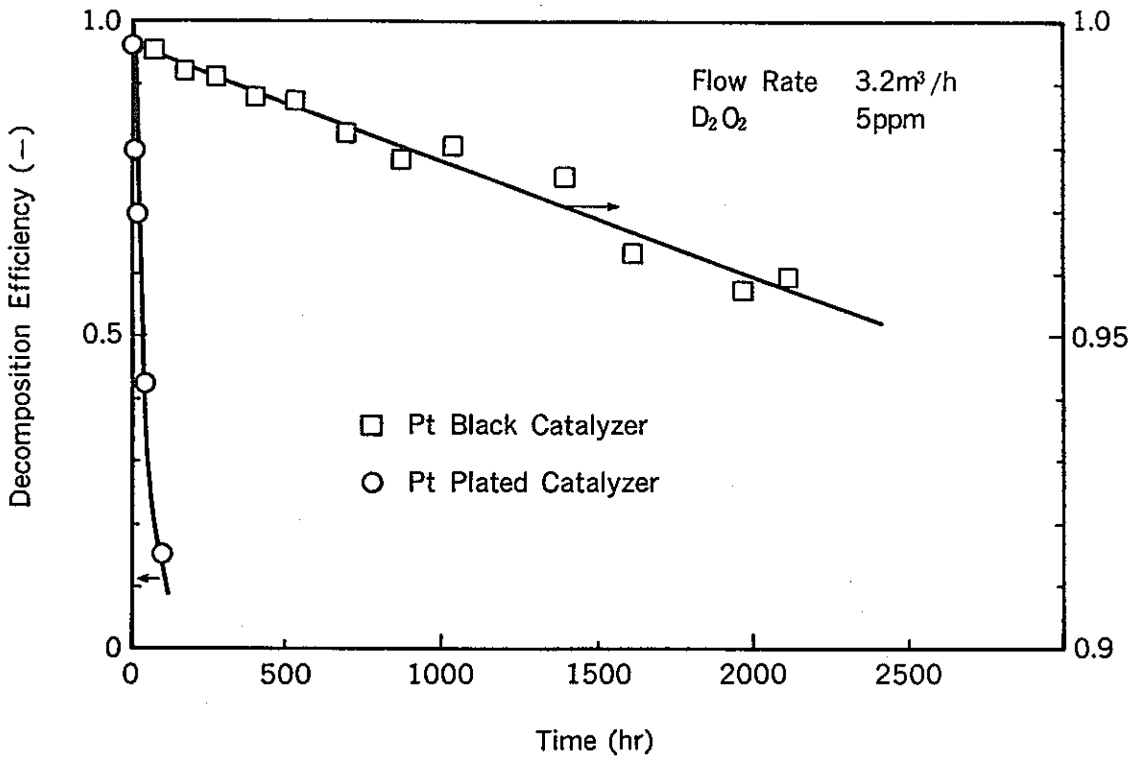

Fig. 3. Degradation of catalyzer in heavy water

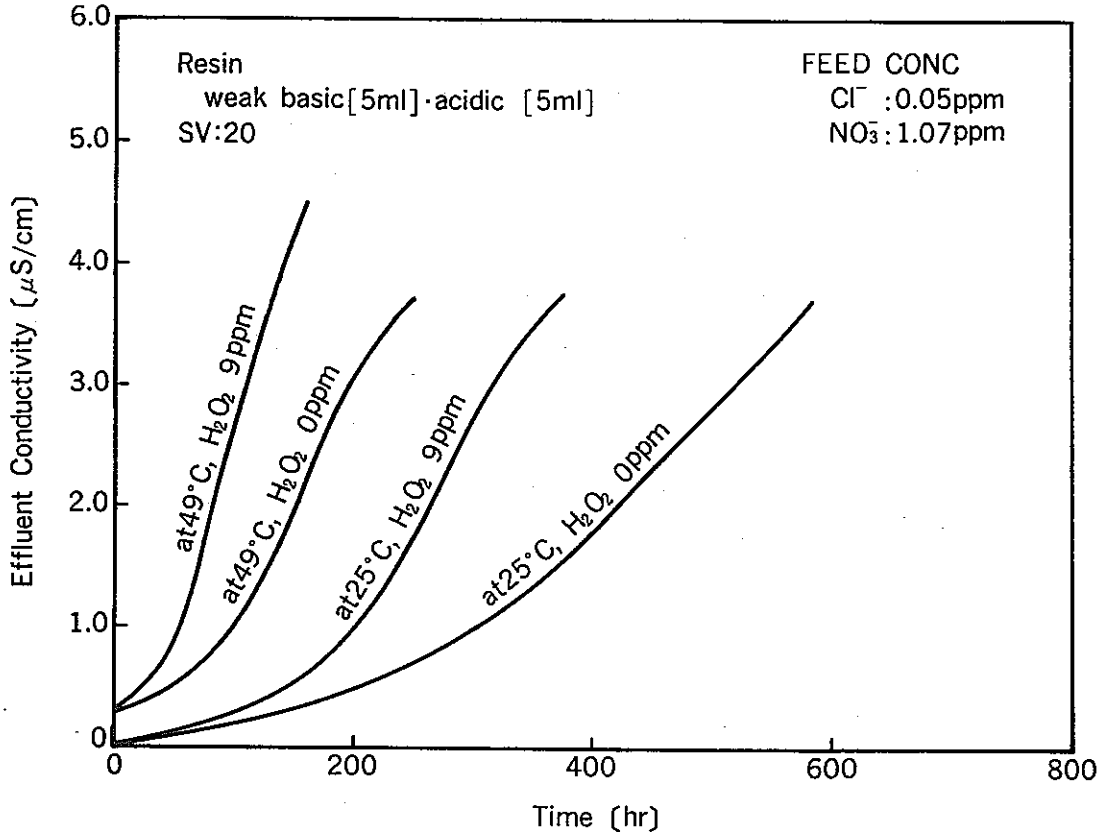

Fig. 4. Effects of temperature and H_2O_2 concentration on the life of resin

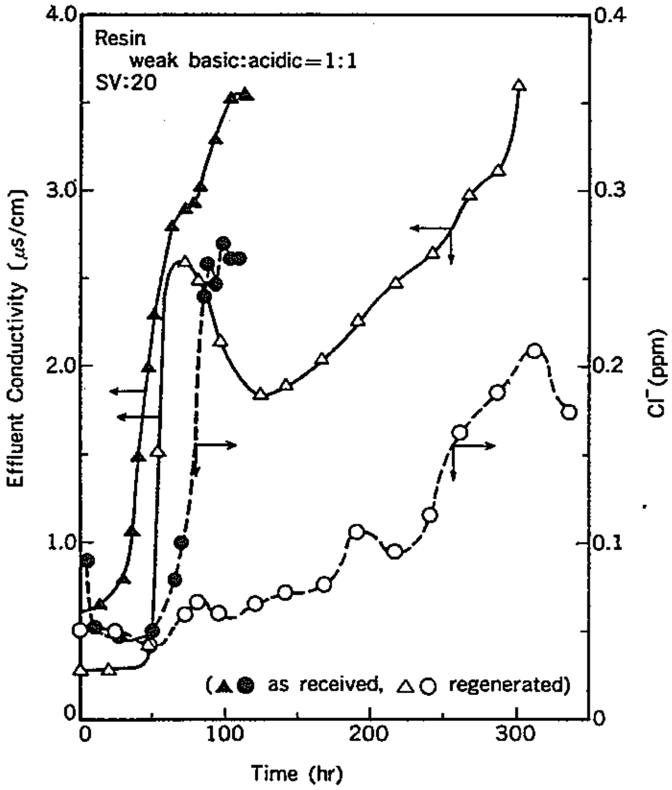

Fig. 5. Effect of regeneration level on conductivity and chloride ion leakage

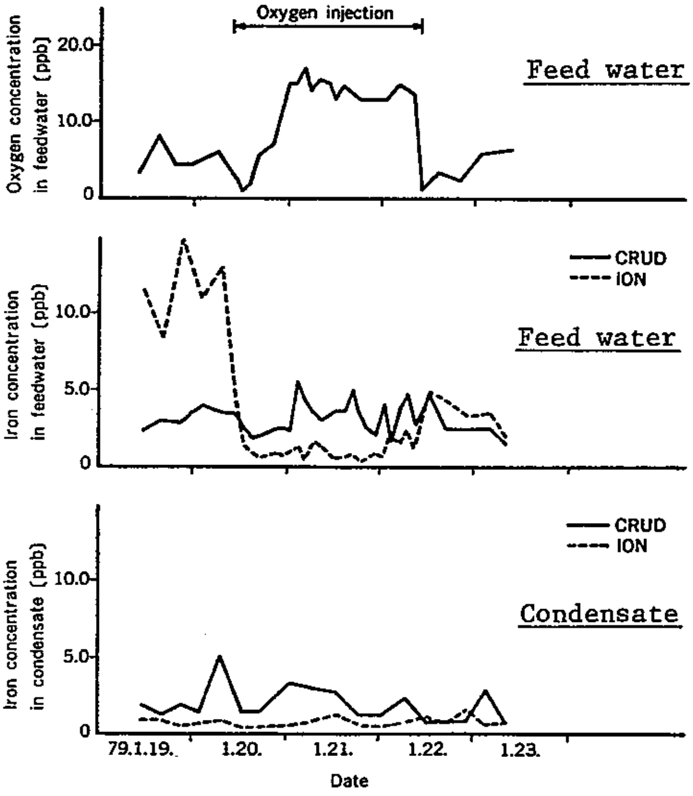

Fig. 6. Effect of oxygen injection into feed water system

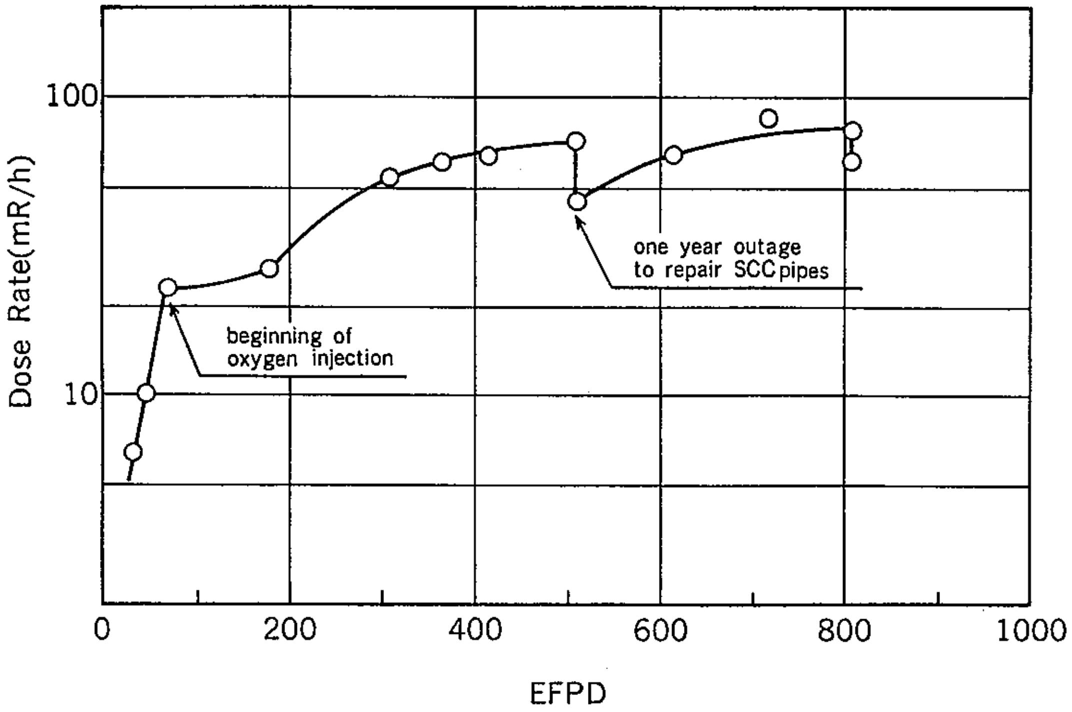

Fig. 7. Variation of dose rate at the outlet of the recirculation pump

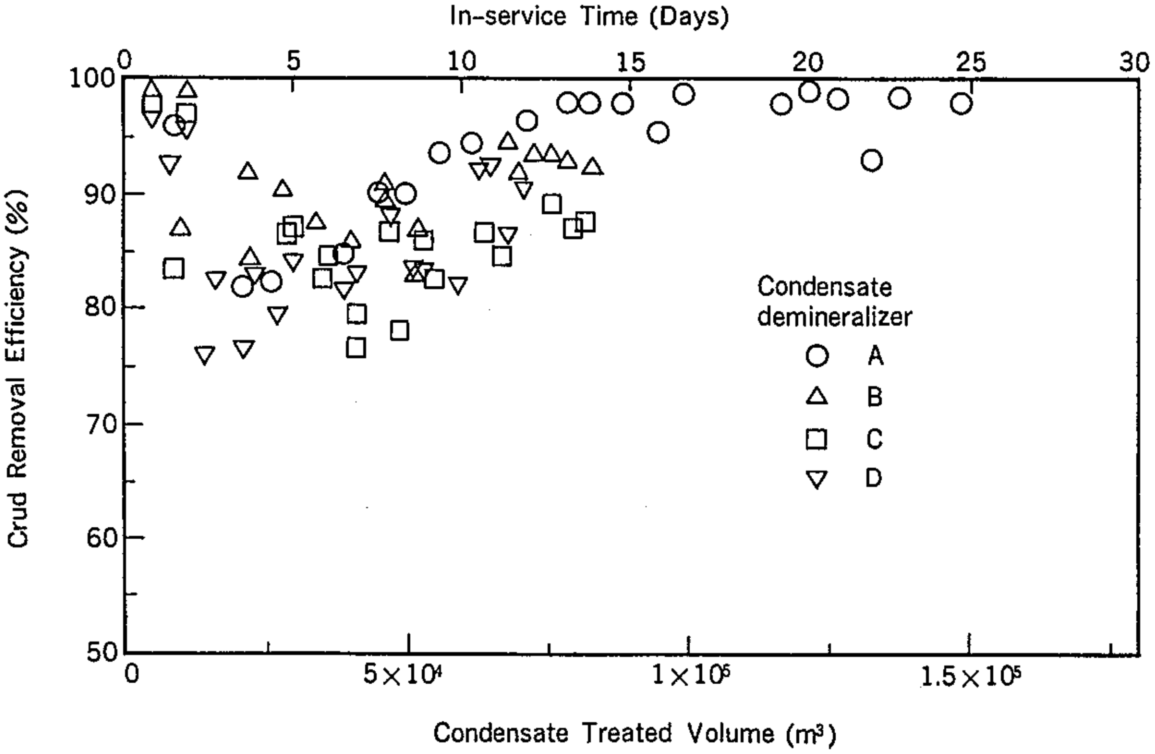

Fig. 8. Crud removal efficiency in condensate demineralizers