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PRIMARY WATER CHEMISTRY IMPROVEMENT FOR RADIATION EXPOSURE REDUCTION AT JAPANESE PWR PLANTS

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ABSTRACT

Radiation exposure during the refuelling outages at Japanese Pressurized Water Reactor (PWR) Plants has been gradually decreased through continuous efforts keeping the radiation dose rates at relatively low level. The improvement of primary water chemistry in respect to reduction of the radiation sources appears as one of the most important contributions to the achieved results and can be classified by the plant operation condition as follows.

- Hot Functional Test (HFT): $H_2 + LiOH$ added chemistry
 - Dissolved Hydrogen (DH_2): 30 cc-STP/kg- H_2O
 - Lithium (Li): 0.5 ppm
- Power operation: pH control of 7.3 ± 0.1 at $285^\circ C$ ($Li_{max} = 2.2$ ppm)
- Shutdown: Low DH_2 control (≈ 0.5 cc-STP/kg- H_2O)

The effectiveness of the above improvements was verified and radiation levels at Japanese PWRs are expected to decrease further with the elapsed operation time.

INTRODUCTION

The purposes of PWR primary water chemistry are to assure the integrity of the component materials and fuel cladding, together with minimizing the out-of-core radiation field.

Fortunately, in the past there have been no such integrity problems in the primary side. That is why, the main concern of the primary chemistry has been focused on the reduction of the radiation field. Particularly, pH control has been considered as an important measure to suppress the transfer of the corrosion products (CP) and as a result, to reduce the radiation sources. Several investigations on the pH control improvement have been done in Japan, so far. Some of these results are described below. This paper touches also the state of other chemical control improvements at Japanese PWR.

The following three points are important to reduce the radiation sources:

- (1) to suppress CP generation by minimizing the corrosion rate;
- (2) to suppress CP activation by controlling CP transfer;
- (3) to reduce CP inventory by removing CP from the primary system.

Further on, each item is described in relation to the corresponding plant operational condition.

PRIMARY WATER CHEMISTRY IMPROVEMENTS FOR RADIATION EXPOSURE REDUCTION

Radiation Sources Reduction

Improvement of Chemical Control during HFT (Suppression of CP Generation)

Generally, the initial corrosion rate is rather high. Therefore, in order to suppress both the CP generation and release from the primary component metal surfaces, it is very effective to form more stable oxide film on the component surfaces during the first heat up, prior to the power operation. To fulfil this, the chemistry control during HFT, performed at the end stage of the plant construction, was developed¹ as follows.

Steam Generator (SG) tubes are considered as a main source of the CP generation in PWR. Alloy 600 and Alloy 690 are the materials used respectively in the conventional and the new designed plants. Corrosion studies with these test materials were carried out under the chemical condition, shown in Table 1.

Table 1. Test conditions of HFT simulation

	Deaerated water	added LiOH	added H ₂	added H ₂ +LiOH
Water quality	DO ₂ <10ppb	Li : 0.5ppm DO ₂ <10ppb	DH ₂ : 30cc/kg-H ₂ O DO ₂ <10ppb	Li : 0.5ppm DH ₂ : 30cc/kg-H ₂ O DO ₂ <10ppb
Temperature	286°C (TT600 As Received) 292°C (TT690 As Received)			
Testing time	600 hr			

Ni is a key element, because it is a major constituent of each Alloy and a parent element of ⁵⁸Co. The corrosion data for Alloy 600 are shown in Figure 1. From these data it was found that "H₂ + LiOH added chemistry" provides the best condition to suppress the CP generation from the Alloys.

The oxide composition formed under this chemistry was rich of Cr. In addition, from the comparison between the depth composition profiles of the oxide film on the each test specimen, it was found that the oxide film thickness in this case is the thinnest one. As a result of the above examination, "H₂ + LiOH added chemistry" was considered as the most effective water chemistry for HFT. For the first time this chemistry was applied to Tomari No.1 unit.

Figure 2 shows the comparison between the dose rates of the major components measured at the first refuelling outage of Tomari No.1 and another plant with the similar design but without H₂ +LiOH added chemistry during HFT. Almost all the measured dose rates at Tomari No.1 were lower than those of the other plant, as dose reduction accounted for ~ 40%. The H₂ +LiOH added chemistry contributed to about a half of this dose reduction. Note, that Fe and Ni concentrations in the primary coolant measured during the HFT at Tomari No.1 were also at relatively low level.

Based on the Tomari No.1 experience, the "H₂ +LiOH added chemistry" has been recognized as the most beneficial chemistry for HFT and applied to the new units as follows.

DH₂: 30 cc-STP/kg-H₂O , Li: 0.5 ppm

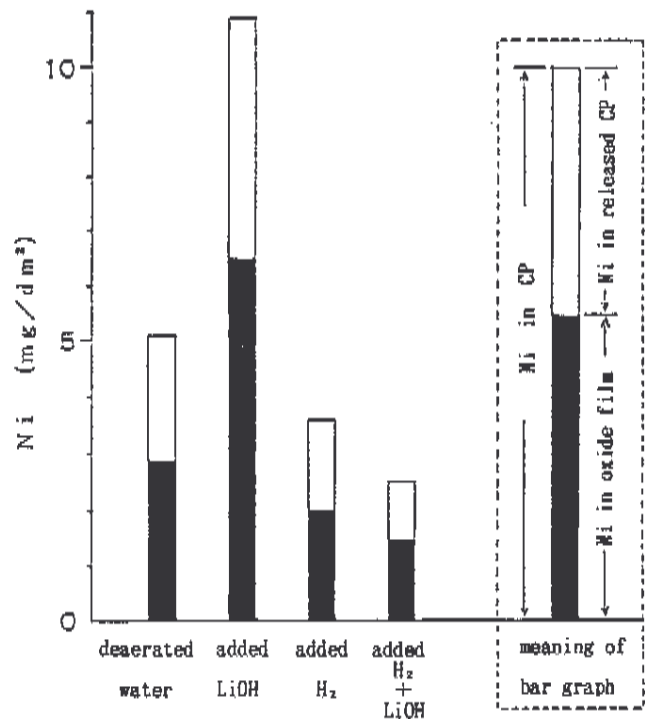


Figure 1. Relations between water quality and amount of Ni in CP (Alloy TT600)

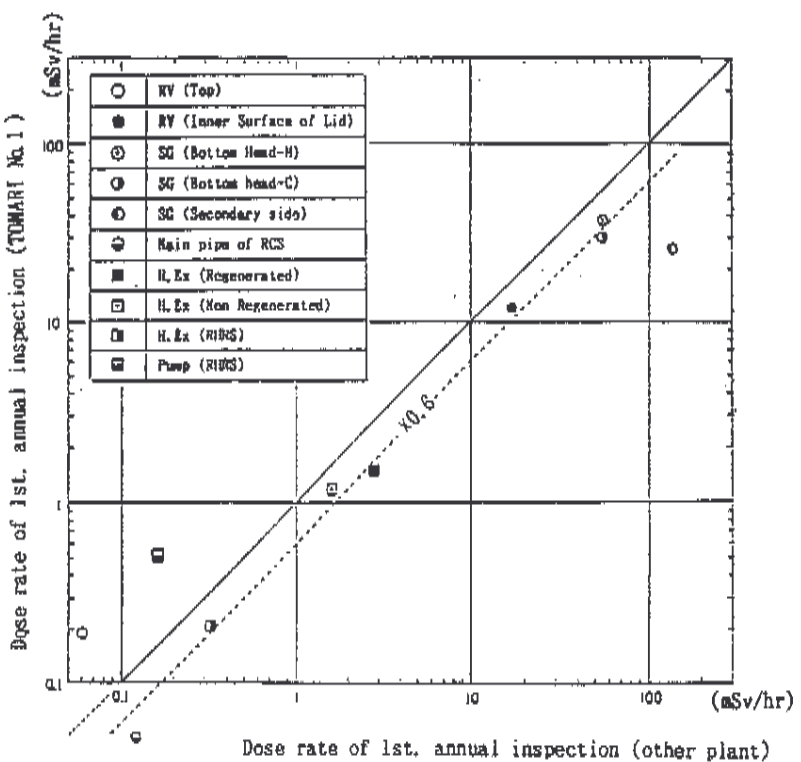


Figure 2. Comparison of dose rates between TOMARI No.1 and other plant

Improvement of pH Control during Power Operation (Suppression of CP Activation)

To suppress the CP activation it is necessary to minimize the crud deposits on the fuel rods and mainly to prevent the precipitation of ionic matter. Many investigations have been carried out worldwide to measure the CP solubility. Abe et al. measured the Fe, Ni, Co solubilities from a model substance (nickel-cobalt-ferrite) simulated the composition of the crud analyzed in the Japanese plants².

Based on the measured data, a solubility formula for each element was derived as a function of pH and temperature. Figure 3-5 represent each solubility curves calculated by those formulas.

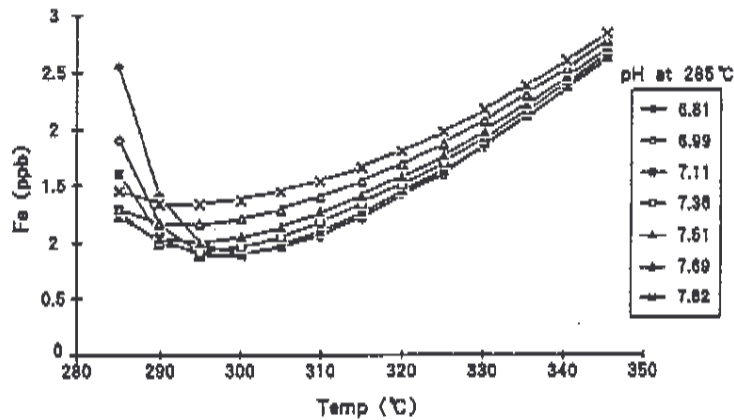


Figure 3. pH and Temp. Dependency of Fe Solubility

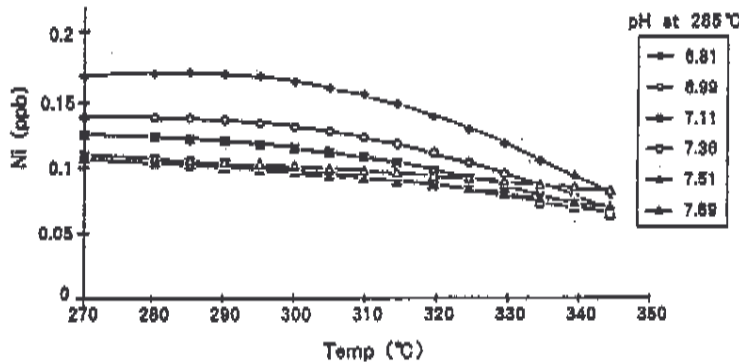


Figure 4. pH and Temp. Dependency of Ni Solubility

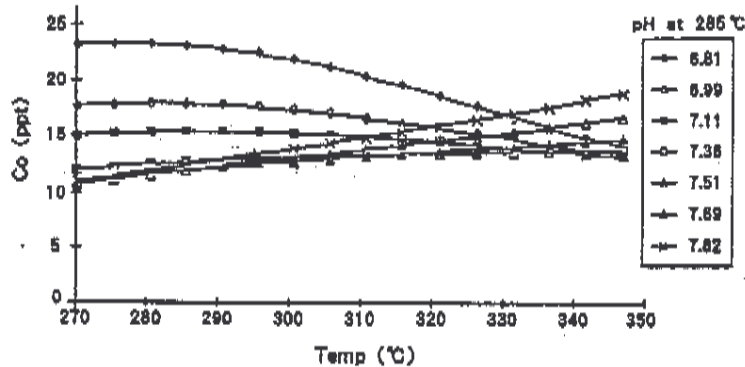


Figure 5. pH and Temp. Dependency of Co Solubility

The optimum pH which minimizes the out-of-core radiation field was estimated by CRSEC code³, where the solubility relations were included. The optimum pH was evaluated of around pH 7.3 at 285°C. Considering the limitation for further rising of Li concentration, three typical cases were selected (Table 2 and Figure 6) to evaluate the actual effectiveness on the out-of-core radiation field reduction.

Table 2. Evaluation Results by CRSEC Code

Case	Target pH at 285	B at BOC (ppm)	B at BOC (ppm)	Upper limit of Li (ppm)	1st cycle	Average
0	6.8	1100	50	2.2	base	
1	7.0	1100	50		-3.1	-6.3
2	7.3	1100	50		-3.8	-11.1

Based on Domestic Data

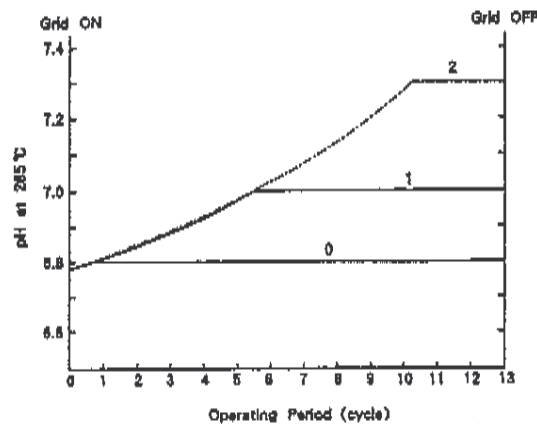


Figure 6. Case study of pH Control

Mitsubishi had recommended pH of 7.0 ± 0.2 at 285°C ($Li_{max} = 2.2$ ppm) as the optimum pH control during the power operation until recently.

At present, a shift to the higher pH control of 7.3 ± 0.1 at 285°C ($Li_{max} = 2.2$ ppm) based on the above results is proposed by Mitsubishi (Figure 7). Now in Japan, many plants operate following this pH control.

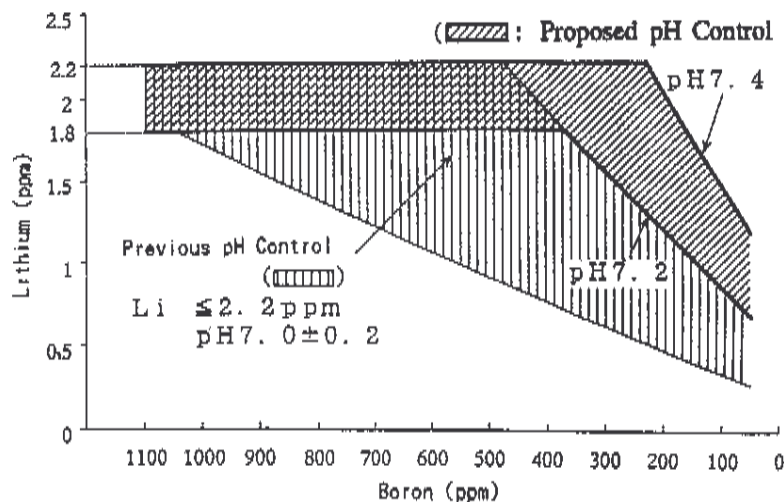


Figure 7. pH Control proposed by Mitsubishi

Removal of CP during Plant Shutdown (Reduction of CP Inventory)

During the plant shutdown, after the plant off-line, Ni and radioactive Co concentrations increase drastically because of the changes in the coolant temperature and chemical condition. Consequently, the ionic CP (Ni, ^{58}Co) levels become more than 10^3 times higher than the observed ones at steady-state power operation. Therefore, the removal of CP by purification of the coolant during the shutdown period is considered as an effective measure to reduce the radiation sources.

A chemical condition which enables the crud to dissolve more effectively was investigated in order to promote the crud inventory reduction. As a result of this investigation, "Low DH_2 control" was developed⁴.

Figure 8 displays our understanding of the crud characteristics and its dissolution reactions in PWR plant during the plant shutdown.

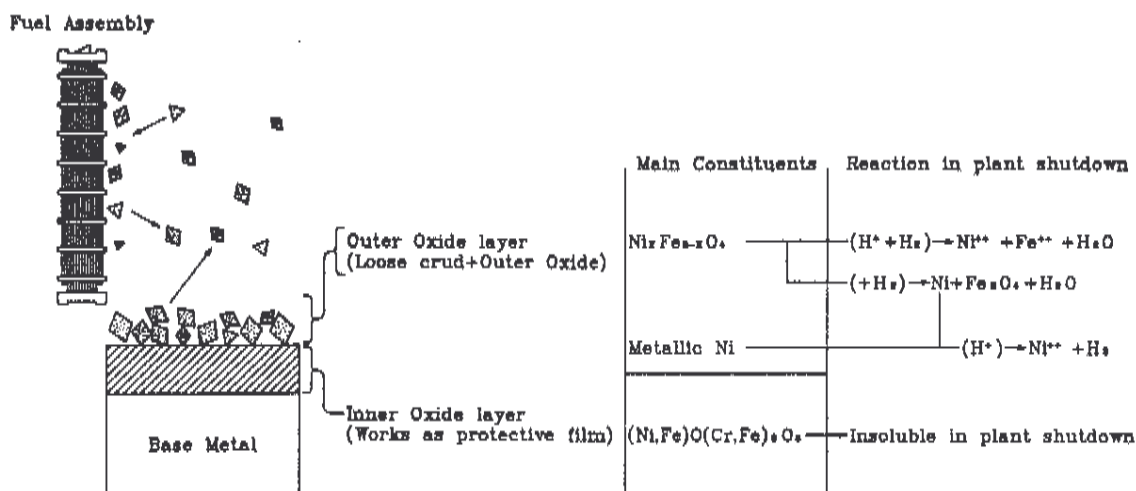


Figure 8. General feature of crud formed in PWR and its dissolution during the plant shutdown process

Using an autoclave test apparatus, Tawaki et al. investigated the dissolution properties of $\text{Ni}_{0.8}\text{Fe}_{2.2}\text{O}_4$ and the metallic Ni under chemical condition which simulates the plant shutdown.

Figure 9 shows the test result. From these data it was found that the trend of Ni dissolution from metallic Ni is very similar to that observed at the actual plants. It was verified that because of the Ni-metal dissolution the concentration of Ni ions increases under the lower DH_2 condition during the simulated plant shutdown. On the other hand, Fe dissolution from $\text{Ni}_{0.8}\text{Fe}_{2.2}\text{O}_4$ exhibits similar trend as the actual plant data. Consequently, it was confirmed that the main source of dissolved Ni during the shutdown condition is metallic Ni, but not nickel ferrite.

Metallic Ni dissolves by reaction of oxidation. Thus, Ni dissolution could be promoted by changing the redox potential to the higher level. To establish such condition, the "Low DH_2 control" (keeping DH_2 concentration about 0.5 cc-STP/kg- H_2O) was developed.

Usual degassing operation takes too long time to reach such a low DH_2 concentration level. Therefore, a hydrogen peroxide (H_2O_2) is injected to the reactor coolant to promote hydrogen degassing.

Figure 10 shows the concentration pattern of ^{58}Co , Ni and Fe measured during "Low DH_2 control". Predicted concentrations correspond to the concentration levels observed under the usual shutdown condition. Data analysis shows that this new control leads to 1.7 times higher Ni dissolution rate than the conventional shutdown chemistry.

The "Low DH_2 control" has recently been applied to many Japanese PWR plants as an effective crud removal operation promoting the crud dissolution during the outage shutdown.

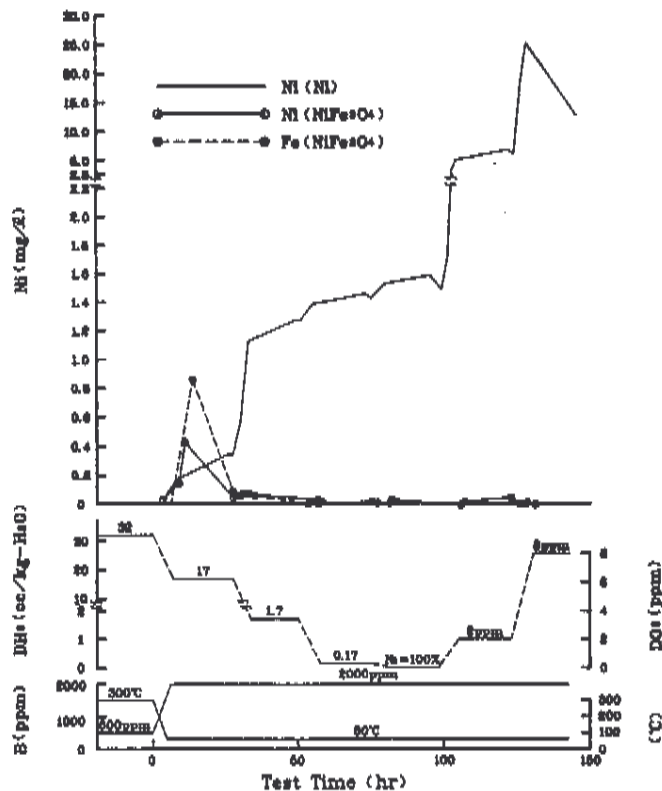


Figure 9. Dissolution of Ni and $Ni_{0.8}Fe_{2.2}O_4$ in boric acid solution simulating plant shutdown

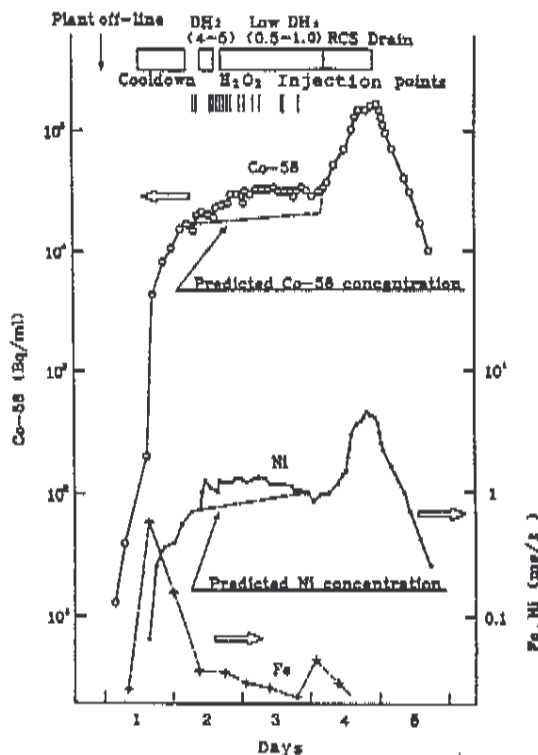


Figure 10. Co-58 and Ni concentration changes during the plant shutdown with low dissolved hydrogen control

Other Improvements

Now, under investigation are several new methods for radiation sources reduction as follows.

- Zn injection
- Other additives (NH₃, etc.)

On the other hand, we have developed the advanced code, called "ACE" for evaluation of crud behavior⁵. This code is capable to model CP transport and has the following range of application:

CP: ⁵⁸Co, ⁶⁰Co, Ni and Co
 Layer: 3 (Loose crud, Outer Oxide and Inner Oxide)
 Region: 14 (Figure 11)

- | | |
|-----------------------------------|---|
| 1 - Hot leg | 8 - Fuel Assemblies (Middle spans) |
| 2 - SG channel head (Hot) | 9 - Fuel Assemblies (Upper spans) |
| 3 - SG tubes (Hot Side) | 10 - Fuel grids & stainless steel inventory |
| 4 - SG tubes (Cold Side) | 11 - Non-irradiated area |
| 5 - SG channel head (Cold) | 12 - RTD (Hot) |
| 6 - Cold leg | 13 - RTD (Cold) |
| 7 - Fuel Assemblies (Lower spans) | 14 - RTD (Return) |

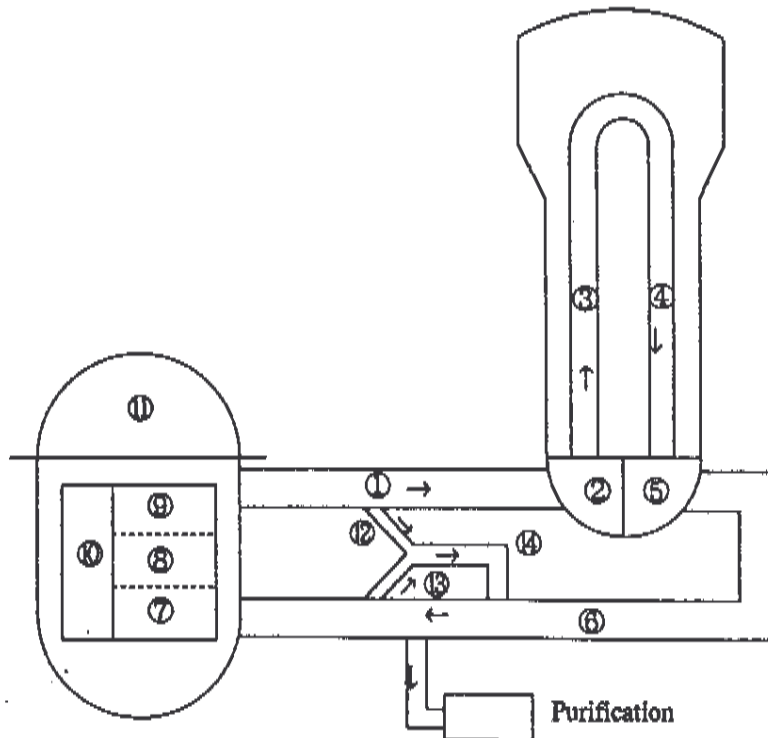


Figure 11. ACE code regions of PWR primary system

Radiation Exposure at Japanese PWRs

As mentioned above, primary water chemistry has been gradually improved to promote the radiation reduction. As a result of these efforts, radiation sources have been considerably reduced.

Figure 12 shows the radiation exposure at the first refuelling outage in Japanese PWRs. From this trend, the effectiveness of plant design and the above chemical control improvements on radiation exposure reduction were verified. Figure 13 displays the trend of SG channel head dose rates and the effectiveness of the improvements for two plants⁶.

It is believed that future primary water chemistry improvements would further decrease the radiation sources and associated with them radiation exposure rates.

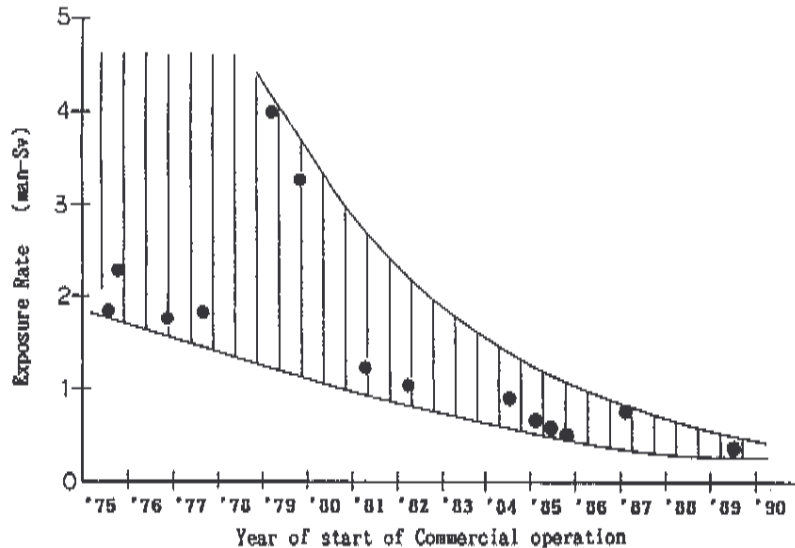


Figure 12. Radiation Exposure during 1st Refuelling Outage

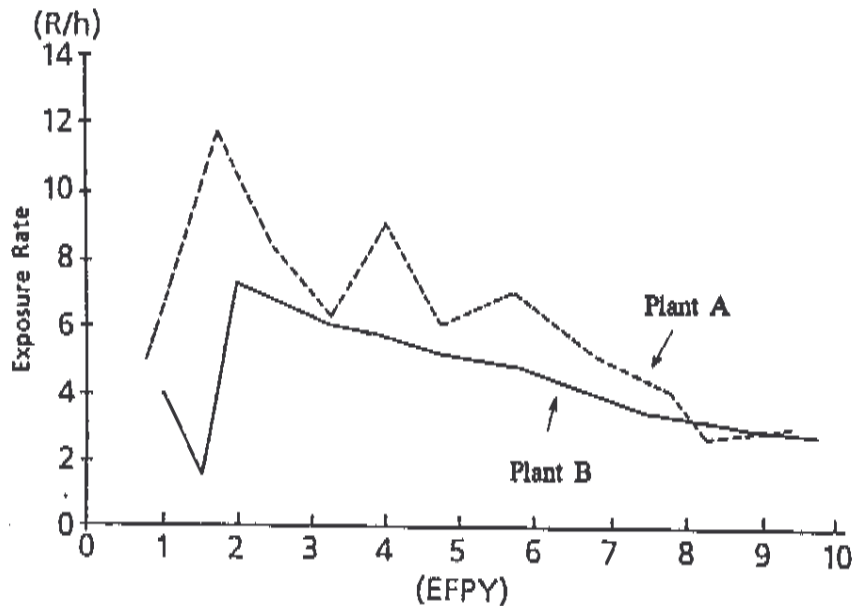


Figure 13. SG Channel Head Exposure Rate

CONCLUSIONS

The following improvements of primary water chemistry in respect to the radiation sources reduction in Japanese PWRs have been done.

- Improvement of the Chemical Control during HFT (Suppression of CP Generation)
- Improvement of pH Control during Power Operation (Suppression of CP Activation)
- Removal of CP during Plant Shutdown (Reduction of CP Inventory)

The effectiveness of above improvements was confirmed by the exposure trends.

Now, under investigation are several new methods for radiation sources reduction, such as Zn and other additives injection.

REFERENCES

1. Yamada, E., Suzuki, S., Hirao, T., Hashimoto, Y., Hisamune, K., and Yokoyama, J., "Corrosion Rate Reduction by Chemistry Control during Hot Functional Test," in *1991 JAIF International Conference on Water Chemistry in Nuclear Power Plants*, pp. 151-156, Japan Atomic Industrial Forum, Inc., Fukui, Japan, April 1991.
2. Abe, K., Mizusaki, H., Ohta, H., Hemmi, Y., Umehara, R., Ooshima, S., Fukuda, F., and Kasahara, K., "Solubility Measurement of CRUD and Evaluation of Optimum pH," in *1991 JAIF International Conference on Water Chemistry in Nuclear Power Plants*, pp. 599-603, Japan Atomic Industrial Forum, Inc., Fukui, Japan, April 1991.
3. Oshima, S., Kasahara, K., Kanda, T., and Nishimura, T., "Evaluation of Corrosion Product Release Using CRSEC Code," in *1988 JAIF International Conference on Water Chemistry in Nuclear Power Plants*, Vol. 2, pp. 468-473, Japan Atomic Industrial Forum, Tokyo, Japan, April 1988.
4. Tawaki, S., Koyasu, T., Katayama, Y., Yokota, T., Hisamune, K., and Saigusa, M., "Improvement of Shutdown Chemistry for Outer Oxide Layer Removal," in *1991 JAIF International Conference on Water Chemistry in Nuclear Power Plants*, pp. 168-173, Japan Atomic Industrial Forum, Inc., Fukui, Japan, April 1991.
5. Kasahara, K., and Nishimura, T., "Advanced Evaluation Code for Crud Behavior in PWR," in *Annual Meeting of the Atomic Energy Society of Japan*, p. 578, Kobe, Japan, October 1993.
6. Makino, I., Hino, Y., Yamauchi, S., and Fukuda, F., "Water Chemistry Control of PWR Nuclear Power Plant," *J. Thermal and Nuclear Power*, Vol. 43, No. 10, pp. 186-202, October 1992.

Author Biography

Elchi Nishizawa is a Senior Engineer with Mitsubishi Atomic Power Industries, Inc. He has 17 years experience at the MAPI's Omiya Technical Institute as a engineer on R&D in the field of PWR primary water chemistry. He was responsible for the water chemistry control during the three start-up tests at Ikata 2, Tomari 1 and Ohi 3 PWR plants. Currently, he is involved in evaluation of radiation sources reduction effectiveness and related computer analyses. He has a B.Sc. in Chemical Engineering from the University of Kyoto, Japan.

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