# Approach of Hitachi for Dose Rate Reduction

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Abstract

In this report, the radiation dose rate reduction methods developed thus far are briefly summarized, and recent topics are discussed as well. In this context, needs for the clarification of deposition mechanism of radioactivity on piping based on the role of oxide films are stressed.

## １．INTRODUCTION

Dose rate reduction of reactor components is one of the main issue for maintaining nuclear power plants effectively as well as safely. From this recognition, many efforts have been devoted worldwide to development of dose rate reduction methods thus far. In recent years, occupational dose exposure of workers in Japan is in the highest level in the world. This can be attributed to several factors including restrictions on operation cycle length and the adoption of on line maintenance. Though, generally speaking, environmental dose rate in Japanese plants is in the low level compared with worldwide statistics, it would be desirable to reduce the dose rate of reactor components further. In this respect, water chemistry plays an important role in controlling the dose rate environment of nuclear power plants. As a BWR maker in Japan, Hitachi has also evaluated the radiation dose behaviour on the piping and developed various techniques for dose rate reduction from the point of view of water chemistry.

In this report, the methods developed thus far are reviewed and recent topics are also shown.

## ２．DOSE RATE REDUCTION METHODS

The deposition behaviours of radioactivity on piping surfaces are quite complicated that careful consideration is required. Basically, radioactivities are incorporated in oxide film formed on the piping surface, and become the source of radiation dose rate. Therefore, we need to reduce the deposition amount of radioactivity into the oxide film. As is well known, deposition amount of radioactivity($\Gamma$) on piping surface is described by the following simplified equation.

$$d\Gamma/dt = \delta \cdot C - \lambda \cdot \Gamma, \qquad (1)$$

Here, t, $\delta$, $C$ and $\lambda$ are time, deposition rate coefficient, concentration of radioactivity in coolant and decay constant, respectively. This equation reveals the deposition amount $\Gamma$ is increased in proportion to $\delta$ and C. Based on the relation, we can understand that there are two approaches to suppress the deposition amount $\Gamma$; one is reduction of radioactivity concentration (C) in coolant and the other is the suppression of deposition rate coefficient($\delta$) into the oxide film.

In Table 1, various methods developed thus far are summarized. The methods are categorized into two groups: one is to be applied in construction or replacement phase of plant and the other in operating phase.

In construction phase, low cobalt content materials are adopted in recent new plants(cobalt content is less than 0.05%) and for piping surface polishing technique is applied. However, cobalt based materials are still in use for components such as a valve which is required certain level of hardness. These components are apt to dissolve due to the wear. As the dissolution of valve materials made of cobalt based metal results in a strong source of cobalt radioactivity, Hitachi has developed wear resistive cobalt based materials for valve(Hitachi Hyper Valve). Surely, when the replacement of components of operating plants is planned, low cobalt content materials are generally adopted. After construction is completed, during plant start up testing phase, alkaline prefilming method is applied for carbon steel on which oxide film is formed by controlling pH. This method will be discussed in more detail in the next section.

As for an operating phase, basic approach of Hitachi is to suppress the radioactivity concentration in coolant as low as possible. For this purpose, Fe/Ni ratio control is adopted. This method was initially proposed based on the fact that cobalt in the coolant water is effectively deposited on the fuel rod if the appropriate amount of Fe and Ni are present forming a cobalt ferrite and stabilizing the radioactivity on the fuel surface resulting in the low concentration of radioactivity in coolant. Ordinarily, in the presence of Ni, ferrite components are stabilized by the formation of nickel ferrite. As the number ratio of Fe/Ni in nickel ferrite($NiFe_2O_4$) is two, the ratio for the control is targeted to be larger than two, because there is some uncertainty of appropriate amount of Fe and Ni for formation of nickel ferrite on the fuel surface.

In recent years, reducing environment such as hydrogen water chemistry has been widely adopted to mitigate oxidizing condition of BWR. In this case, it tends that dose rate of pipings are generally increased. This phenomena can be interpreted that under reducing environment chromium based oxides are formed and those oxides easily take cobalt to pile up cobalt radioactivity. For a countermeasure of this process, zinc injection method was developed by General Electric. This method is expected to be effective for reduction of dose rate of piping under reducing water chemistry. However, it should be stressed here that the role of zinc is not so simple for reducing the deposition amount of radioactivity on the piping.

When inspection or repair of piping are considered, usually chemical decontamination process is applied prior to the beginning of the work. In this case, the oxide film on the piping is removed and new oxide films are formed after the plant operation begins. If the operation is going on under the reducing water condition, the re-deposition of radioactivity proceeds quite rapidly and the dose rate of piping recovers the original level or is multiplied by several factors in a short period. The zinc injection is an effective countermeasure for this phenomena. However, there are another approach in which protecting thin film is formed before plant operation. This approach will be shown in the following section.

## 3. ALKALINE PREFILMING

Radioactive ions are incorporated into the growing oxide film on steel through corrosion process. Therefore, it is possible to assume the suppression of corrosion should reduce the buildup of radioactivity. On the basis of this concept, several prefilming methods were proposed, and some have been applied to actual plants. Alkaline prefilming is one of the methods for forming a closely packed oxide film on the surface of piping. Experiments showed that oxide film formed by controlling coolant pH in alkaline region suppress the deposition of radioactivity. In actual plants, the method has been implemented during a start-up testing period.

Alkaline prefilming has been applied to 4 plants thus far. In actual implementations, coolant pH has been controlled to 8.0〜8.5 by passing the coolant water through sodium-type cation resin precoated on RWCU (reactor water clean up system) filer element for about 100 hours, prior to start up test. After one cycle operation of plants, as shown in Fig.1, it was found that the deposition rate of RWCU carbon steel piping with alkaline prefilming was smaller than that without alkaline prefilming, and that however reducing effect on stainless steel was not apparent.

The difference was interpreted by taking into consideration of oxide film characteristics of carbon steel and stainless steel. In the case of carbon steel, only iron based oxides are formed and once formed, the presence of the oxides prevents the further growth of oxides, resulting in the reduction of radioactivity. While, due to the presence of chromium component in stainless steel, Cr rich oxides are formed as well as iron base oxide on the surface of the stainless steel during the prefilming. The chromium rich oxides such as $FeCr_2O_4$ have a strong tendency to incorporate cobalt into the film. These are supposed to be a cause of the difference in deposition behaviors between carbon steel and stainless steel.

## ４．RECENT TOPIC

In recent several years, Japanese BWR utilities have been required a large scale maintenance activities due to a necessity for preventive maintenance of core internals and/or a newly found stress corrosion crackings(SCC) of low carbon content stainless steel. In this activities, inspections and repairs of primary loop recirculation piping(PLR piping) were included. Prior to inspection or repair, chemical decontamination process has been applied and contributed much for occupational exposure reduction. However, it became clear that in some cases the dose rate of pipings recovered in quite short period after plant operation began. As was explained in the preceding section, reducing water condition is one of the biggest cause of radioactivity build-up in the first operating cycle after decontamination: oxide films formed under the reducing water chemistry has characteristic feature to pile up the cobalt radioactivity in the film. One approach to reduce the buildup process is to apply a zinc injection.

However, for this purpose, zinc must be continually injected in coolant and its cost is not negligible. Recently, Hitachi found that after decontamination process radioactivity incorporation in oxide film was quite effectively suppressed by forming a thin closely packed ferrite film on the piping surface. Fig.2 shows the cross sectional view of the formed film on the stainless steel(SUS316L) The films were formed by immersing the test piece in a solution of iron formate($Fe(HCOO)_2$) under control of pH and oxidizing conditions, and temperature was 90℃. The deposition behavior of radioactivity on the test piece is shown in Fig.3, in which the comparison between a test piece as polished and ferrite coated test piece is also shown. The test conditions are simulated HWC in BWR. As we can see, in the case of ferrite coated test piece, the deposition amount is suppressed by about a fifth of the polished test piece. The big merit of this method is that we can easily process the coating by using an existing decontamination equipments, that is, without any major change of the system. This means the chemicals to be used in the both processes are almost the same: hydrazine for pH control and hydrogen peroxide for oxidizing condition control, the only difference is the presence of iron formate for ferrite coating.

The film formation process in actual site implementation is described in the followings:

1) Surface oxide film and CRUDs are removed by chemical decontamination process called HOP(Hydrazine, Oxalic acid and Potassium permanganate).
2) After the decontamination, solutions containing iron formate, hydrazine and hydrogen peroxide are supplied in the decontaminated pipings to coat the ferrite film.
3) The remained solutions are decomposed by using the catalyst column for reduction of waste disposal.
4) Final step is the water cleaning by ion exchange resin.

The process described above is completed without any large additional time consuming, and the total process has been demonstrated by a tenth scale model of actual recirculation piping system.

## 5. SUMMARY

Dose rate reduction methods are reviewed stressing the role of oxide films formed on the surface of the structural components. The control of the oxide film is considered to be an essential factor for a reduction of dose rate of piping. From this point of view, we should further understand the nature of oxide films for developing an effective method of dose rate reduction.

It was found that alkaline prefilming for carbon steel and ferrite coating(Hi-F coat) for recirculation piping were promising methods for dose rate reduction.

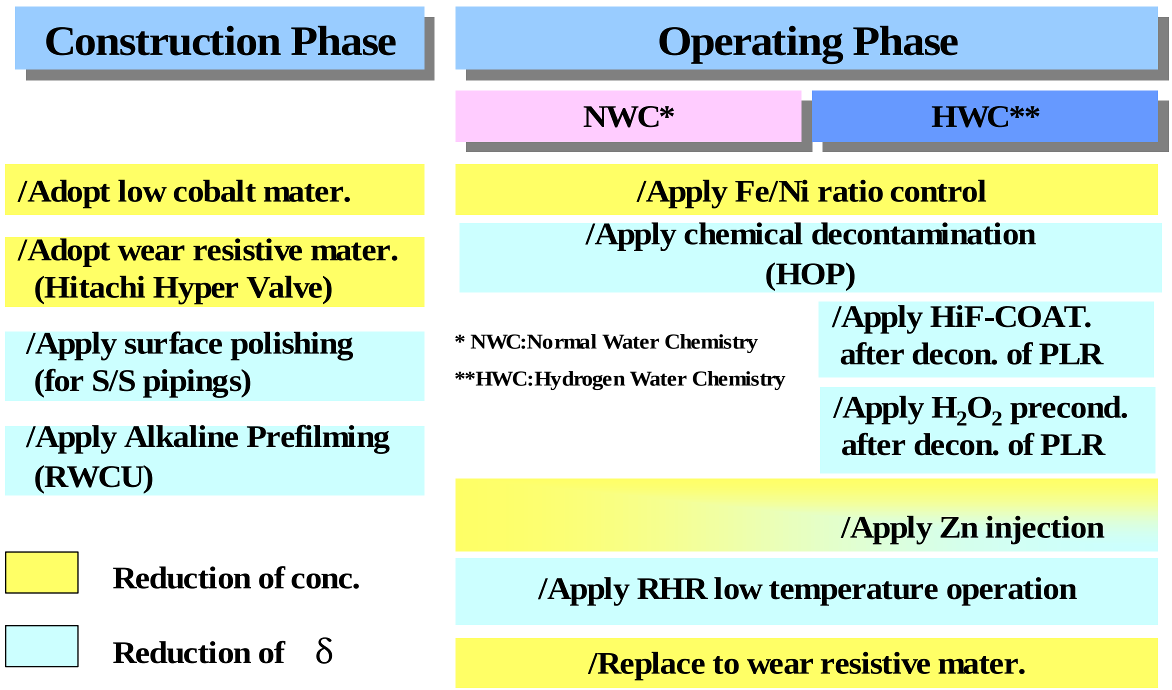
References

1) T. Honda, K. Ohsumi, M. Aizawa., “AN ALKALINE PREFILMING PROCESS FOR THE PRIMARY PIPIG IN A NEW JAPANESE BOILING WATER REACTORS”,*NUCLEAR TECHNOLOGY.,* . **89**, 365 (1990)

2) N.Suzuki, et al., ‘An ABWR Water Chemistry Control Design Concept for Low Radiation Exposure and the Operating Experience at the Fist ABWR’9th International Conference on Water Chemistry in Nuclear Reactor Systems (Avignon,Apr.22-26,2002)

3) N. Usui, M. Fuse, H. Hosokawa, S. Uchida., “Effects of Hydrogen Peroxide on Radioactive Cobalt Deposition on Stainless Steel Surface in High Temperature Water”, *Nucl. Sci. Technol.,* . **42**, 75 (2005)

Table 1 Dose Rate Reduction Methods Hitachi Recommends



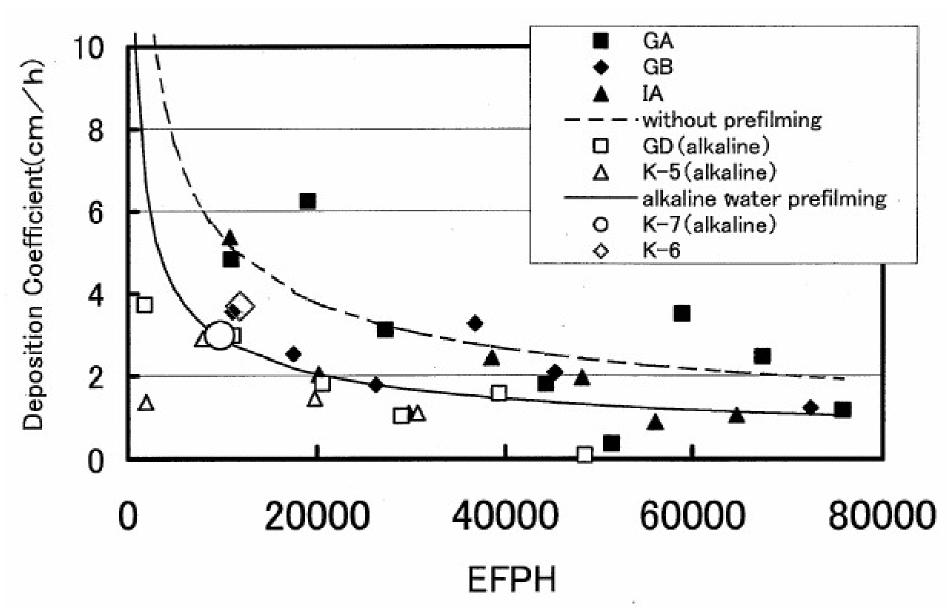




Fig.1 60Co deposition coefficient of RWCW piping

N.Suzuki ‘An ABWR Water Chemistry Control Design Concept for Low Radiation Exposure and the Operating Experience at the Fist ABWR’9th International Conference on Water Chemistry in Nuclear Reactor Systems (Avignon,Apr.22-26,2002)

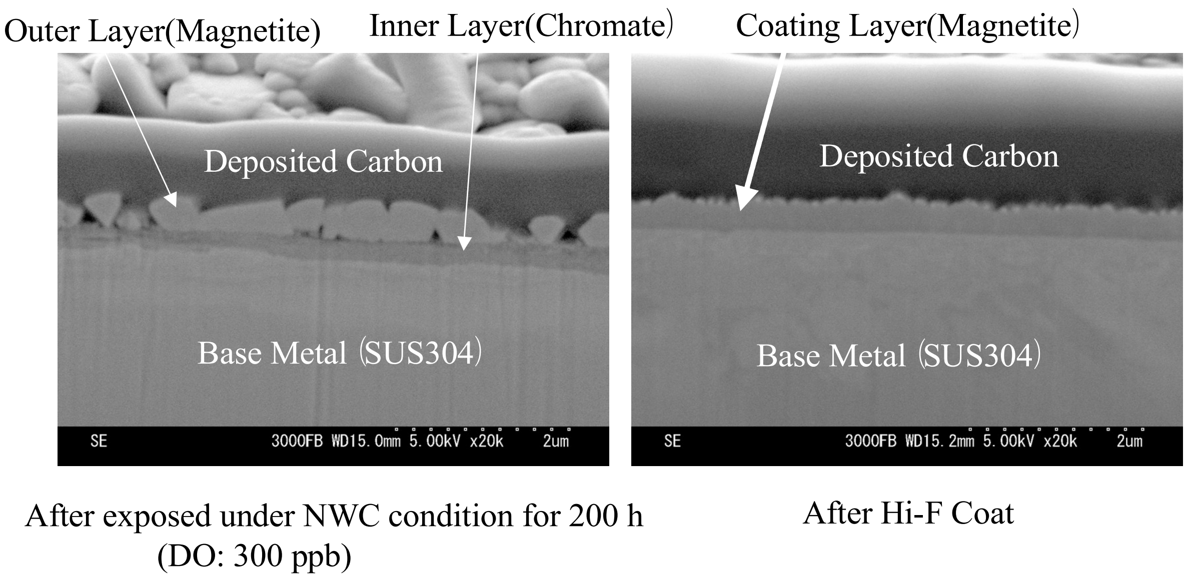



Fig.2 Cross sectional view of the formed film on the stainless steel (SUS304).

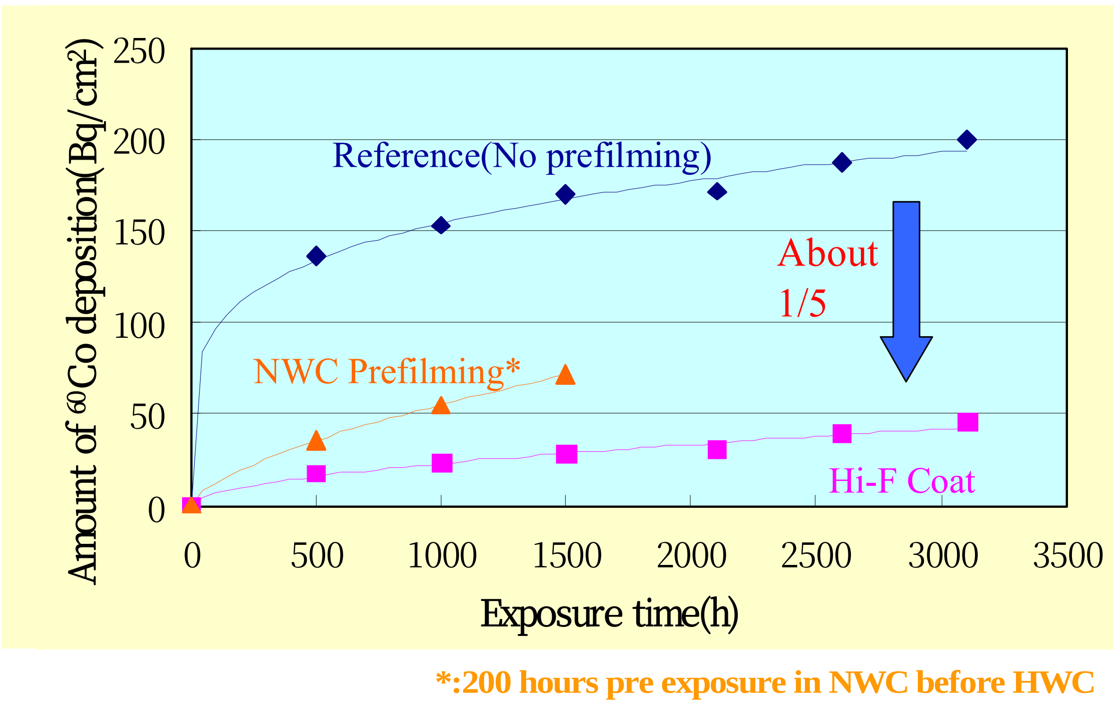



Fig.3 The deposition behavior of radioactivity on the test piece