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OPTIMUM WATER CHEMISTRY IN RADIATION FIELD BUILDUP CONTROL

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ABSTRACT

Nuclear utilities continue to face the challenge of reducing exposure of plant maintenance personnel. GE Nuclear Energy has developed the concept of Optimum Water Chemistry (OWC) to reduce the radiation field buildup and minimize the radioactive waste production. It is believed that reduction of radioactive sources and improvement of the water chemistry quality should significantly reduce both the radiation exposure and radwaste production. The most important source of radioactivity is cobalt and replacement of cobalt containing alloy in the core region as well as in the entire primary system is considered the first priority to achieve the goal of low exposure and minimized waste production. A plant specific computerized cobalt transport model has been developed to evaluate various options in a BWR system under specific conditions. Reduction of iron input and maintaining low ionic impurities in the coolant have been identified as two major tasks for operators. Addition of depleted zinc is a proven technique to reduce Co-60 in reactor water and on out-of-core piping surfaces. The effect of HWC on Co-60 transport in the primary system will also be discussed.

INTRODUCTION

LWR water chemistry parameters are directly or indirectly related to the plant's operational performance and for a significant amount of Operation and Maintenance (O&M) costs. Obvious impacts are the operational costs associated with water treatment, monitoring and associated radwaste generation. Less obvious is the important role water chemistry plays in the magnitude of drywell shutdown dose rates, fuel corrosion performance and materials degradation. To improve the operational excellence of the BWR and to minimize the impact of water chemistry on O&M costs, General Electric has developed the concept of Optimum Water Chemistry (OWC).¹ The "best practices" and latest technology findings from the U.S., Asia and Europe are integrated into the suggested OWC Specification.

It is believed that reduction of radioactive sources and improvement of the water chemistry quality should significantly reduce both the radiation exposure and radwaste production. A number of known technologies and options are available to reactor operators, including cobalt source reduction, iron reduction, depleted zinc addition, control of ionic and organic impurities in reactor water, and decontamination, etc. A plant specific computerized cobalt transport model has been developed to evaluate various options in a BWR system under specific conditions. Some key parameters in OWC specification and the effect of hydrogen water chemistry (HWC) on radiation buildup control will be discussed in this paper.

OPTIMUM CHEMISTRY GOALS AND PROPOSED KEY CHEMISTRY PARAMETERS IN BWR COOLANT

The goals of optimum coolant chemistry in BWRs and proposed key chemistry parameters are given in Tables 1 and 2, respectively. Each of these goals and proposed limits has been demonstrated to be achievable in an operating BWR in Asia, Europe and the United States. However, no one reactor has yet achieved all of the optimum parameters, simultaneously. Major objectives of this paper are to discuss how the proposed chemistry parameters are related to optimum chemistry goals and to outline a strategy to meet those proposed chemistry limits.

Table 1. Optimum Water Chemistry Goals in BWRs

Parameter	Goals
IGSCC	No new crack initiation or growth (<0.01 in/yr)
Annual collective radiation exposure	<100 man-Rem/reactor
Annual radwaste volume	<110 m ³
Fuel clad corrosion	No fuel failure due to water chemistry effect

Table 2. Proposed Key Chemistry Parameters in BWR Coolant

Parameter	Feedwater	Reactor Water
Iron	0.1 to 0.5 ppb	*
Cobalt	< 2.0 ppt	*
Copper	<50 ppt	<0.5 ppb
Nickel	<30 ppt	*
Sulfate	<50 ppt	<5 ppb
Chloride	<50 ppt	<5 ppb
Co-60	**	<2 Bq/g
Conductivity	**	<0.08 μ S/cm
Electrochemical corrosion potential	**	Value that achieves goals of -No new IGSCC crack initiation -Minimum crack growth rate <0.01 in/yr

*Unspecified, controlled by feedwater limits

**Unspecified, controlled by reactor water limits

SHUTDOWN RADIATION FIELD BUILDUP CONTROL

The primary source of radiation field buildup on out-of-core surface is Co-60, with the exception of a few GEZIP plants where Zn-65 is also an important contributor to the recirculation piping radiation field. The activity transport process is a complex chemical reaction which can be affected by many water chemistry parameters. A semi-empirical phenomenological model has been developed to describe and calculate the corrosion product transport in the BWR primary system.² This model is presented in a block diagram shown in Figure 1. Model calculations are often very useful to estimate the relative contribution of each cobalt source in the system to the radiation field buildup. The effects of iron and other chemistry parameters can also be evaluated. It is well understood that radiation field buildup in many locations in the primary system may not occur by a similar mechanism nor at the same rate. In order to achieve the goal of reducing the radiation field to a very low level,

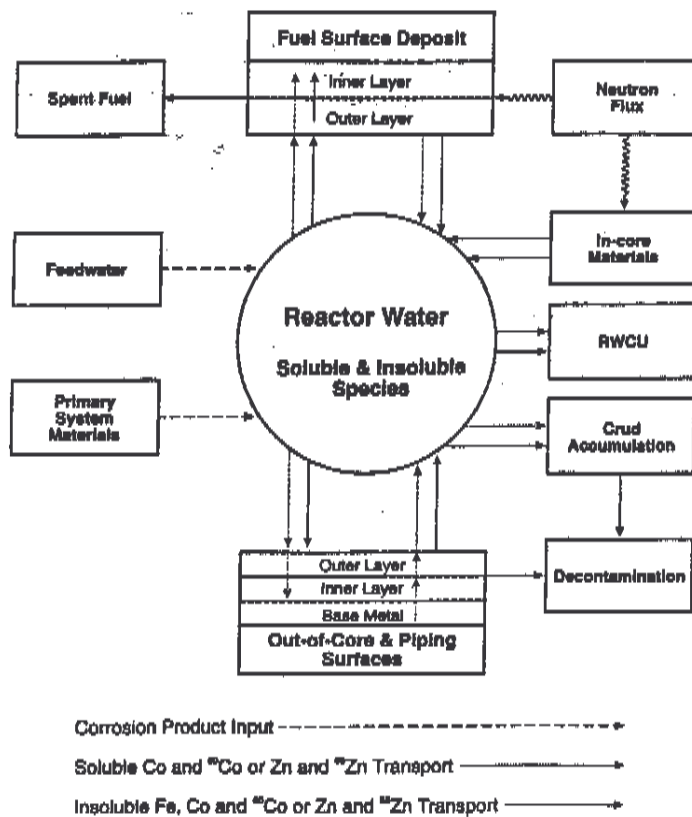


Figure 1. Schematic block diagram of corrosion product transport model

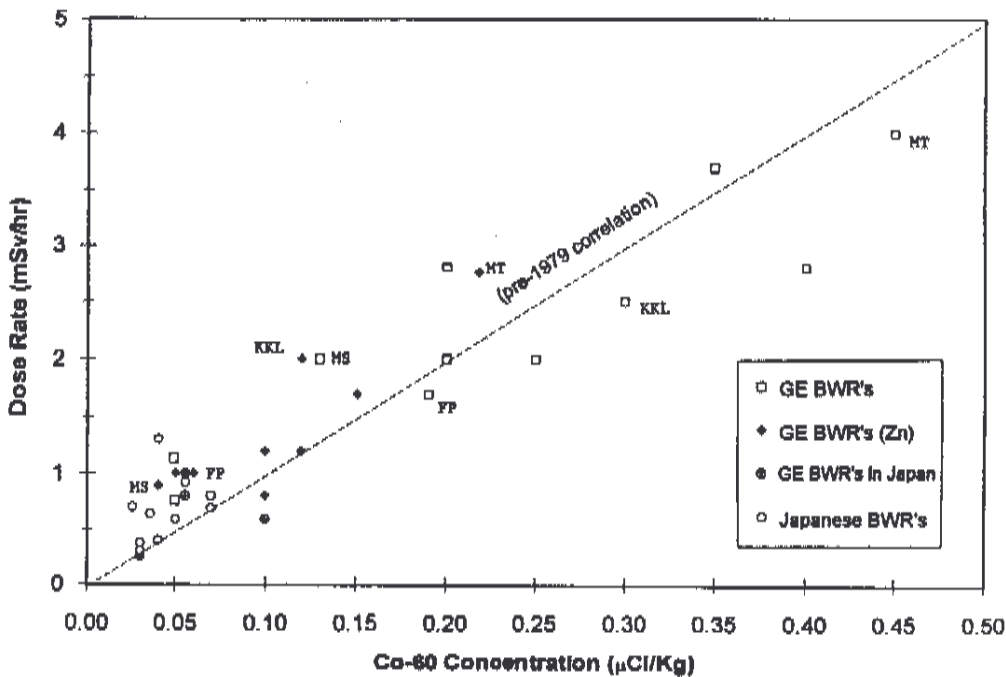


Figure 2. Correlation between soluble Co-60 concentration in reactor water and recirculation pipe dose rates

reduction of cobalt sources is the first priority, but other factors affecting the Co/Co-60 transport processes should be considered equally important. Some major factors are briefly described below:

Cobalt Source Removal

Figure 2 shows the relationship between the soluble Co-60 concentration in the reactor water and recirculation pipe dose rates. Note that the contact piping dose rate is linear with the soluble Co-60 concentration, equilibrium dose rates at approximately 100 mR/hr per 0.1 μ Ci/kg. Hence, one of the first priorities of reducing radiation field is to remove the sources of cobalt. There are several sources of cobalt including cobalt alloys and structure materials containing cobalt as impurities. All sources must be addressed, but the cobalt bearing materials in the core region should be given highest priority, because they are the most obvious contributors to the Co-60 in reactor water.

The benefit of replacing cobalt alloys or materials with non-cobalt or low cobalt materials may be very plant specific. A reliable cobalt transport model should be used to estimate the relative contribution of each component to the radiation field buildup. A cobalt replacement guideline has been published by Ocken.³ One area easily overlooked are the feedwater heaters and steam dryer. If replaced, it is important that these large surface area components be made from material of controlled, low cobalt impurity concentration.

Control of Iron Input

In addition to producing Fe-55, Fe-59 and Mn-54 activities after neutron activation on fuel surfaces, iron plays an important role in Co/Co-60 transport and radiation field buildup in the primary system. A comprehensive review of the subject has been reported by Lin.⁴ Iron acts as carrier of Co/Co-60 in reactor water; iron enhances Co and other transition metal ions (e.g. Zn, Ni, Cu) deposition on fuel surfaces, but it also enhances Co-60 or Zn-65 release from fuel surfaces when excessive iron is present on fuel surfaces. Excessive iron in water carrying the activities also create high radiation hot-spots in low flow regions in the primary system, including equipment drain lines, LPRM housing, vessel bottom, etc. Insufficient iron in fuel deposit will result in high soluble activities in reactor water and enhance the activity deposition on piping walls.

The optimum concentration of iron in feedwater should be controlled at \sim 0.5 ppb or lower, depending on the levels of transition metal ions in water. It has been hypothesized in GE cobalt transport model⁵ that the iron crud (α -Fe₂O₃ is normally found in the fuel deposit) containing Co-60 may form a tight deposit by reacting with adequate transition metal ions which provide the "gluing" power for the bulky iron oxide deposit to form the stable mixed metal ferrites (spinel) in the deposit. In most U.S. domestic BWRs with relatively higher iron concentrations an increase of transition metal ions such as Zn⁺² would certainly help reducing Co-60 release from the fuel deposit (see more below in Zn Addition). On the other hand, in most of the new Japanese plants the feedwater iron concentration is very low (<0.1 ppb). Under this condition NiO becomes the major component in the fuel deposit which is not stable and Co-58 and Co-60 are released easily from the fuel deposit. To minimize the cobalt activity release, Japanese have implemented a technique to inject the synthesized iron crud in the feedwater system to increase the Fe/Ni ratio up to approximately 5 (but the total Fe concentration is limited to 0.5 ppb) so that the Fe/Ni ratio in the fuel deposit is approaching 2, which is the stoichiometric ratio of Fe/Ni in the Fe and Ni mixed oxide in a spinel form, NiFe₂O₄.

Iron constitutes approximately 80% of the corrosion product oxides in the reactor coolant and fuel deposit. The majority of iron originates from corrosion of balance of plant carbon steel components in the steam/condensate and feedwater systems and is delivered to the reactor by the feedwater. To control the feedwater iron input, the first priority is to identify and eliminate the sources of iron. If the sources cannot be all eliminated, at least it is practical to identify key source terms and mitigate them by replacing the key components with corrosion resistant materials and/or coating the surfaces with corrosion resistant materials. The iron in the condensate upstream of the condensate treatment system should be effectively removed by improving the crud removal capabilities. For plants having deepbed demineralizers, addition of pre-filter is possible. Backwashable filters would generate minimum radwaste, while a greater majority of iron originates from corrosion of balance of plant carbon steel components in

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Zinc Addition

Control of radiation field buildup in BWRs by zinc addition in the feedwater was first introduced by Marble⁶ in 1986. It was hypothesized that soluble zinc inhibits the corrosion of stainless steel and thereby reduces the buildup of Co-60 on the piping surfaces. Currently, there are 13 plants operating worldwide utilizing zinc addition for shutdown radiation control.

Laboratory test results⁷ confirmed that the Co-60 deposition rate is significantly lower in water containing 5-15 ppb of soluble zinc. The deposition rate was found even lower under HWC conditions with same levels of soluble zinc in water. Zinc ions appear to not only reduce the corrosion rate but also provide competition with Co-60 ions for the reaction sites on the corroding surface. With the overwhelming concentration ratios ($Zn/Co \geq 100$), Co-60 is easily prevented from depositing on the stainless steel surfaces. In reactor experience, maintaining a constant level of zinc in reactor water has been proven to be an effective means to control the piping radiation field buildup on out-of-core piping. One important effect of zinc addition, which was not considered initially was the reduction of Co-60 concentrations in reactor water. A factor of 2-3 reduction in Co-60 has been observed in several reactors implementing GEZIP (GE Zinc Injection Process) (Figure 3). Some reactor data are also indicated in Figure 2. The reason for this effect has been discussed previously in the last section. This significant benefit of zinc addition is probably equally as important as the reduction of piping contamination in reactor operation.

After several years of GEZIP experience in operating BWRs, it has been observed that the Zn-65 activity, produced by the $^{64}Zn(n,\gamma)^{65}Zn$ reaction in natural zinc, can not be ignored. The benefits of zinc addition on Co-60 radiation buildup control are diminished by the presence of Zn-65 in some plants: much higher Zn-65 activity contribution to piping dose rates than expected (20-80%), particularly under HWC conditions; tramp Zn-65 found around the site in unwanted places; shutdown releases have increased the Zn-65 concentration in reactor water during shutdown cause higher than desired refueling floor dose rates; and the radwaste Curie content can be significantly increased. To eliminate these unwanted problems, it is recommended that Zn-64 depleted zinc oxide (DZO) replace the natural zinc in reactor applications. The Zn-64 content in depleted zinc is reduced from ~48.6% in natural zinc to ~1%. The quantity of DZO requirement in a reactor is very plant specific, mostly depending on the iron concentration in the feedwater and reactor water. Therefore, reduction of iron input in a high crud plant should significantly reduce the cost of using DZO.

Reduction of Ionic Impurities

As described earlier, the main mechanism of Co-60 deposition is incorporation of soluble Co⁶⁰ into the corroding stainless steel surfaces and the Co-60 deposition rate is known to be related to the stainless steel corrosion rate. Certain ionic impurities are known to enhance the corrosion rate of stainless steel and, therefore, increase the activity buildup rate. Laboratory experiments⁷ have clearly demonstrated that when common laboratory chemicals like Na₂SO₄, H₂SO₄, NaOH were used as additives in water significantly higher Co⁶⁰ buildup rates were observed (see Figure 4). Thus, minimizing the impurity input to maintain the reactor water conductivity at $\leq 0.08 \mu S/cm$ is essential to reduction of radiation field buildup. An exception would be the higher conductivity condition that accompanies zinc addition.

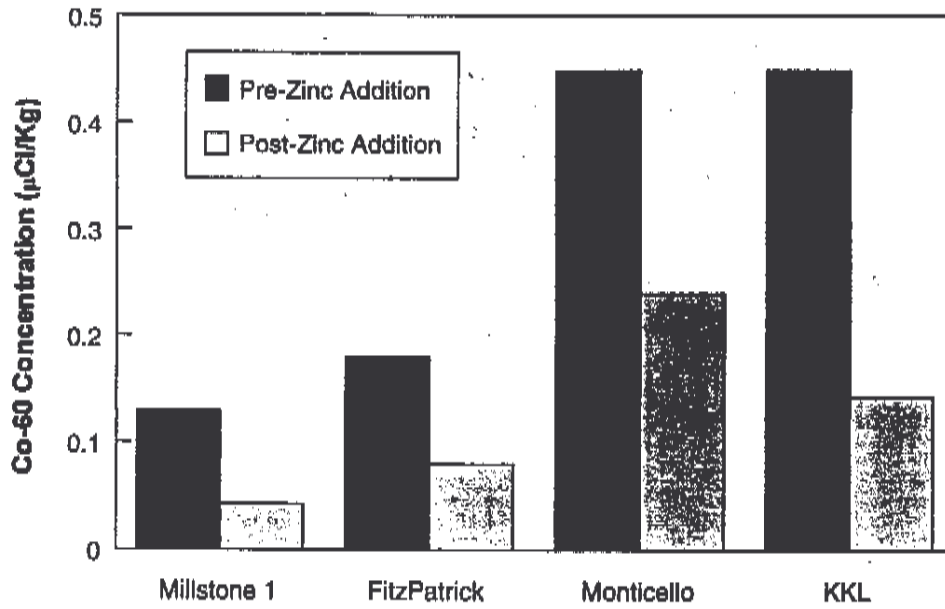


Figure 3. Fuel cycle average total Co-60 concentration in reactor water before and after implementation of zinc addition at four operating BWRs

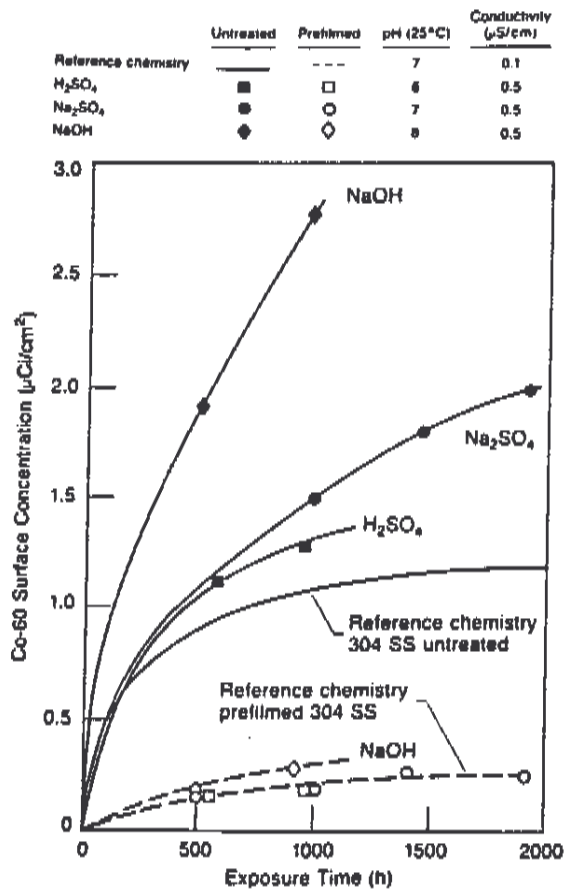


Figure 4. Effects of ionic impurities on Co-60 activity deposition on stainless steel test samples under NWC conditions

Role of Decontamination

The decontamination, if performed safely and efficiently, is probably the quickest way to reduce the radiation fields inside the drywell working area. However, the cost, the schedule, the radwaste produced in decontamination process, and the exposures associated with the performance of decontamination are significant enough to prohibit some operators from accepting it as a routine procedure. Furthermore, the surfaces after decontamination are generally corroding much faster without an established oxide film to protect from recontamination of Co-60 from reactor water. Consequently, the dose rates on decontaminated piping surfaces generally increase quickly within a cycle back to a pre-decontamination level. The decontamination operation may save some exposures immediately following the decontamination, but the plant may require repeated decontamination operations in every outage maintenance schedule. The decontamination vendors and plant operators should carefully consider some ways to minimize the recontamination problem. A strategy involving decontamination coupled with DZO injection is probably the cost effective way to radically limit subsequent contamination.

There are only a few chemical procedures which have been qualified for decontamination in BWR piping systems. The major concern is the attack of chemicals on the base metal of system materials. Some discussion on the issues of corrosion and the role of chemical decontamination in radiation control can be found elsewhere.⁸ More recently, a feasibility study on full system decontamination has been performed, and the results of this study are reported in Ref. (9) and summarized in Ref. (10).

Effect of HWC

Laboratory test results⁷ have shown that Co-60 deposition on stainless steel will probably be slightly enhanced by switching from NWC to HWC. The activity buildup rate is more profound under cyclic HWC/NWC conditions (see Figure 5).¹¹ In some U.S. reactors after switching from NWC to HWC, an increase in piping dose rate has been reported, but some plants including a few foreign plants have shown very minimal or no effect.¹² In some plants enhanced release of Co-60 activity has been observed, probably due to frequently changing HWC/NWC conditions. In the one plant which is adding higher levels of hydrogen for protection of internals, and which is also using GEZIP, an enhanced Zn-65 activity deposition on piping surfaces has also been observed. All these phenomena may be related to the result of oxidation/reduction processes, occurring in the oxide film as water chemistry environment is changed. While these effects are believed to be transient, they may persist for several cycles till corrosion films and solubilities stabilize under reducing conditions. A study is in progress to evaluate the HWC effect on radiation buildup through laboratory experiments and assessment of plant data.¹¹

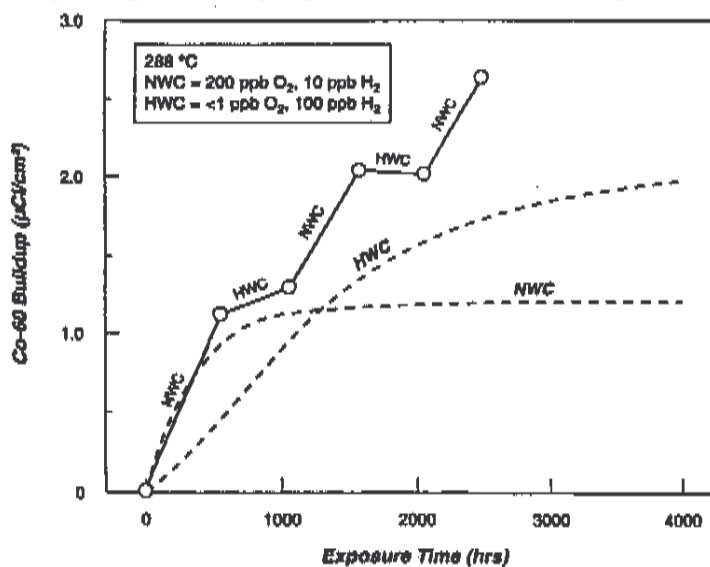


Figure 5. A comparison of Co-60 activity deposition on stainless steel samples under NWC, HWC and cycling between NWC/HWC

SUMMARY AND CONCLUSION

The concept of optimum water chemistry can be realized in radiation field reduction. Among the key chemistry parameters, cobalt and other metallic and ionic impurities should be minimized. The feedwater iron input should be controlled at 0.1 to 0.5 ppb to ensure a lower activity release rate from the fuel surface deposit. Addition of zinc in reactor water would also decrease the Co-60 concentration in reactor and activity buildup on out-of-core surfaces.

Cobalt/Co-60 activity buildup model calculations are essential to define effective approaches to control and reduce radiation field buildup.

Effects of HWC on radiation field buildup have been observed, but the magnitude may be minimized with source term reduction and proper operation procedures.

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Author Biography

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