WATER CHEMISTRY – ONE OF THE KEY TECHNOLOGIES
FOR SAFE AND RELIABLE NUCLEAR POWER PLANT OPERATION

Uchida S.¹, Otoha K.² and Ishigure K.³
¹ Japan Atomic Energy Agency, Tokai, Japan
² Saitama Institute of Technology, Okabe, Japan
³ Japan Atomic Power Co., Tokyo, Japan

Abstract

Water chemistry control is one of the key technologies to establish safe and reliable operation of nuclear power plants. Continuous and collaborative efforts of plant manufacturers and plant operator utilities have been focused on optimal water chemistry control, for which, a trio of requirements for water chemistry, a) better reliability of reactor structures and fuels, b) lower occupational exposure, and c) fewer radwaste sources, should be simultaneously satisfied. The research committee related to water chemistry of the Atomic Energy Society of Japan has played important roles to enhance improvement in water chemistry control, to share knowledge and experience with water chemistry among plant operators and manufacturers, to establish common technological bases for plant water chemistry and then to transfer them to the next generation related to water chemistry. Furthermore, the committee has tried to contribute to arranging R&D proposals for further improvement in water chemistry control through road map planning.

1. Introduction

Two of the most important roles of water in nuclear power plants (NPPs) are acting as an energy transfer medium and as a neutron moderation medium. Water chemistry control of the cooling water in NPPs is based on experiences acquired in fossil power plants (FPPs) and is one of the key technologies to maintain reliability against the structural materials of plants [1]. Four major requirements for NPPs are 1) higher safety, 2) higher reliability, 3) greater economic acceptability, and 4) fewer environmental impacts. Continuous and collaborative efforts of plant manufacturers and plant operator utilities have been focused on satisfying these four major requirements. One of the more effective procedures to satisfy them is optimal water chemistry control, for which the following trio of requirements, a) better reliability in reactor structures and fuels, b) lower occupational exposure, and c) fewer radwaste sources, should be simultaneously satisfied [2]. The results of collaborative efforts have been applied as the optimal water chemistry control for BWRs and PWRs of the Japanese Improvement and Standardization Program (JISP) [3].

Plant water chemistry is affected by a plant’s unique systems, materials used and operational histories, which leads to difficulties in establishing the trio of requirements for water chemistry with common water chemistry control. Each plant must be operated with its own optimized water chemistry. For this, sufficient knowledge on plant systems, materials and operation as well as a sufficient technological basis for the chemistry are required for plant chemists and their supervisors. Since 1982, the research committee related to plant water chemistry has worked to promote two purposes in the Atomic Energy Society of Japan (AESJ).

i) To improve the technological basis of plant water chemistry by encouraging frequent discussions.

ii) To share knowledge and experience with water chemistry among plant operators and manufacturers and to transfer them to the next generation related to water chemistry.

In the paper, major roles of water chemistry in plant safe and reliable operation and major contributions of the Water Chemistry Research Committee to water chemistry improvement and its future investigative subjects are introduced.

2. Latest concerns of water chemistry in light water reactors

2.1 Major features of water chemistry in NPPs

Distributions of materials in contact with the coolant differ in BWR and PWR systems. In each system, uniformly controlled cooling water is in contact with different materials, which complicates corrosion problems. Corrosion behaviors are much affected by water qualities and differ according to the combinations of water qualities and the materials themselves. Different combinations of materials and different water chemistry controls for both systems cause different interactions between materials and cooling water and then, consequently different material problems. The interactions of materials and cooling water in the BWR primary cooling system, PWR cooling systems have been detailed in reference [4].
temperature water causes corrosion of structural materials, which leads to adverse effects in the plants, e.g., increasing shutdown radiation, generating defects in materials of the major components and fuel claddings, and increasing the volume of radwaste sources [5].

2.2 Optimal water chemistry
In order to control the adverse effects, it is essential to understand corrosion behaviors of structural materials and then to control them in BWR and PWR systems. Corrosion behavior is much affected by the combinations of water qualities and materials. In order to minimize the adverse effects, optimal water chemistry control has been proposed as shown in Fig. 1 [3].

2.3 Technology competition and cooperation
Plant manufacturers vie with each other to establish optimal water chemistry for their respective plants. At the same time, they wished to establish common technical bases for the optimal water chemistry and, towards this end, they presented their experience with plant water chemistry and research results related to water chemistry at domestic and international conferences. The Water Chemistry Research Committee of AESJ has continuously played important roles to facilitate technical discussions and information exchange on water chemistry of NPPs (Table 1). Through periodic meetings of the committee (5-6 times a year), annual and fall meetings of the AESJ and international conferences, many discussions were carried out to share plant water chemistry experiences (Fig. 2). The committee also contributed to compiling and publishing water chemistry data bases as a water chemistry handbook [5]. Both competition and cooperation richly contributed to improved water chemistry. Major targets for water chemistry improvement and their achievements for LWRs are summarized in Fig. 3. Undesirable plant availability factors, large numbers of defective fuel assemblies and large occupational exposures were recorded in past periods but they have been mitigated drastically.

<table>
<thead>
<tr>
<th>Table 1 Activities of Water Chemistry Research Committee</th>
</tr>
</thead>
<tbody>
<tr>
<td>Research Committee</td>
</tr>
<tr>
<td>---------------------</td>
</tr>
</tbody>
</table>

Figure 1 Optimal water chemistry control

Figure 2 Presentations on water chemistry at AESJ meeting

Figure 3 Major targets for water chemistry improvement and achievements
3. Major achievements with water chemistry in LWRs

3.1 Shutdown radiation control for occupational exposure reduction

The major radioactive nuclide to determine the shutdown dose rate around the BWR primary cooling system is $^{58}$Co. Ferrous ions in the water are easily oxidized to become oxide particles (so-call iron crud) and fed into the reactor water with cobalt ions to deposit on the fuel surface, where the deposits are activated by neutron irradiation to become harmful radioactive corrosion products, e.g., $^{60}$Co. Cobalt-60 on the fuel dissolves into the reactor water and some of it deposits on the piping inner surface to cause a radiation field. In order to suppress cobalt activation, iron crud input has been controlled by oxygen injection to control ferrous ion release from carbon steel of the feed water pipes and by application of a dual polishing system to control iron crud from the condensate water. As a result of the improvement, iron crud concentration was decreased and then crud $^{60}$Co radioactivity was decreased. Unfortunately, too low an amount of iron crud caused interruption of $^{60}$Co re-deposition on the fuel surface and then ionic $^{60}$Co radioactivity increased [6].

In order to minimize shutdown dose rate, two approaches are proposed for competition (Fig. 4) [7]. One is optimal iron crud concentration control and the other is ultra low iron crud and higher nickel ion concentration control. When iron concentration is controlled in a suitable region to suppress crud $^{60}$Co and ionic $^{60}$Co at the same time, total $^{60}$Co radioactivity is suppressed at the minimum value and then $^{60}$Co deposition can be controlled at the minimum level. When iron crud concentration is suppressed as low as possible, ionic $^{60}$Co radioactivity increases but at the same time nickel ion concentration also increases, which causes a lower cobalt deposition rate on the piping inner surface and then $^{60}$Co deposition can be controlled at the minimum level. These different approaches for dose rate reduction with the same final goal are now being applied for operating power plants.

The major radioactive nuclide in the PWR primary cooling system is $^{58}$Co. It is obtained from the nickel alloy of the steam generator tubing, which is activated on the fuel surface and then released into the reactor water again to accumulate in the steam generators and to cause the shutdown dose rate. Suitable pH control and Zn injection are the latest countermeasures minimizing the shutdown dose rate. Surface treatment for prevention of radioactive corrosion products formation is also a common technology applied in LWRs [5].

3.2 Evaluation and control of corrosive conditions

One of the most serious problems with structural materials in BWRs is intergranular stress corrosion cracking (IGSCC) of stainless steel [8]. IGSCC is an undesirable result of overlapping effects of materials, stress and water chemistry factors. Corrosive conditions in the BWR primary cooling system are determined by corrosive radiolytic species, e.g., $\text{O}_2$ and $\text{H}_2\text{O}_2$. In the PWR primary and secondary systems, oxidant could be reduced by adding hydrogen or hydrazine, while in BWRs, hydrogen injection for fully oxidant suppression was not applicable due to hydrogen loss through the main steam line [8]. However, the experience with reduced oxidant concentration in the recirculation water has led to development of hydrogen water chemistry (HWC) to moderate corrosive conditions in the recirculation line and the lower reactor plenum. With increasing hydrogen injection, oxygen concentration measured at the sampling point decreases rapidly and, at the same time, the main steam line dose rate (MSDR) increases gradually (Fig. 5) [8]. The optimal hydrogen injection amount is determined to suppress oxygen concentration without serious increase of MSDR.

![Figure 4 Optimal water chemistry for dose rate reduction](image1)

![Figure 5 Effects of HWC on corrosive conditions](image2)
One of the most common indexes for corrosive conditions to evaluate the effects of HWC in BWR plants is electrochemical corrosion potential (ECP) [8]. ECP is determined by a combination of factors: these are concentrations of oxidants and specimen surface conditions. Measured ECP for HWC was still too high to mitigate IGSCC in the optimal hydrogen concentration determined by oxygen concentration. The gap between the measured ECP and measured oxygen concentration shown in Fig. 5 is explained by the contribution of $H_2O_2$ to ECP especially at high $H_2$ injection rate [9].

Concentrations of oxidants change along the recirculation flow path so that the corrosive conditions differ between locations [7]. The only point to determine oxidant concentrations along recirculation flow is at the end of the sampling line installed in the recirculation line, where water is cooled down and depressurized for the probe type oxygen detector. In order to determine the oxidant distribution in the primary system, theoretical models have been prepared to calculate the concentration distribution. Non-linear rate equations were calculated to obtain the concentration distributions of radiolytic species throughout the primary coolant [10]. The concentrations of $H_2O_2$ and $O_2$ were calculated and for both normal water chemistry (NWC) and hydrogen water chemistry (HWC) conditions, $H_2O_2$ concentration was high enough to determine ECP by only $H_2O_2$ [11].

In PWR primary coolant, addition of sufficient amounts of $H_2$ has suppressed $O_2$ concentration, thus avoiding problems related to corrosion. Recently, it was reported that primary water stress corrosion cracking (PWSCC) of Ni-base alloy was caused by $H_2$ in the coolant. In order to avoid PWSCC, optimization of $H_2$ concentration is necessary and a water radiolysis model for PWRs has been developed. The PWR radiolysis model is much simpler than that for BWRs because transfer of radiolytic species from the water phase to the steam phase is not considered, but prior to the radiolysis calculation, high temperature pH determined by Li and B concentrations should be calculated and irradiation effects of $\alpha$ rays from the $^{10}B(n,\alpha)^7Li$ reaction as well as $\gamma$ rays and neutrons should be considered [12].

4. Latest experience with water chemistry

Even when technologies in water chemistry control have matured to satisfy the trio of requirements for water chemistry, the challenges of new subjects often appear and additional efforts are required for plant chemists and engineers. Latest experiences with problems related to water chemistry are introduced in this section.

4.1 Increasing occupational exposure

Tremendous reduction of shutdown radiation level around the primary cooling systems and then reduction in occupational exposures was recorded as shown in Fig. 3. Unfortunately recent increases in man power for inspection of major component and structures have caused a gradual increase in occupational exposures both for BWRs and PWRs [13]. Latest occupational exposures at Japanese LWRs showed rather high values with increasing trends. The shutdown dose rate has not increased but it was quite obvious that man power for inspection and maintenance jobs around the primary cooling systems has increased for aging plants. Technological innovations in water chemistry for further dose rate reduction are desired to reduce occupational exposure while accepting the increasing labor for inspection and maintenance.

4.2 Stress corrosion cracking of BWR core shrouds

As a result of application of SCC resistant stainless steel, type 316L stainless steel, to the BWR primary cooling systems, it had been believed that SCC would be a distant subject of water chemistry control and it might appear only in aging plants. Unfortunately, a lot of cracks have been identified in the core shrouds of more than 10 Japanese BWRs [14]. It was reported that the cracks were initiated as transgranular stress corrosion cracking (TGSCC) at the surface which was hardened by mechanical treatment and they propagated as IGSCC. The major countermeasure for IGSCC of type 316L stainless steel was stress improvement of the hardened surface zone. Water chemistry was also expected to contribute to mitigation of material IGSCC. Inspection and modification of core shrouds in plants also led to increasing occupational exposures.

4.3 Flow accelerated corrosion of feed water piping

Piping rupture in the Mihama-3 NPP feed water line is a typical example of flow accelerated corrosion (FAC). Local thinning of a piping wall was observed [15]. Turbulence of flow caused acceleration of local corrosion and then local thinning caused sudden rupture. FAC is not limited to PWRs, but has also been reported in FPPs. FAC in single phase flow of the BWR feed water system has not been reported.
Ferrous ions released from carbon steel of the feed water piping caused radioactive corrosion product formation in the reactor water. In order to cut ferrous ion concentration in the feed water, a small amount of oxygen was injected into the feed water line. This lowered condensate water conductivity and then, ferrous ion concentration; when oxygen injection was stopped, ferrous ion concentration increased rapidly (Fig. 6) [13]. Corrosion of carbon steel is considered as one effect of FAC. Because oxygen injection was applied in the early stage of plant operation, localized thinning has not been observed yet. The threshold oxygen level to suppress FAC in BWR conditions (pure neutral water) was 20 ppb [16]. It was reported that a sufficient amount of oxygen can suppress FAC under high pH conditions in FPPs [17]. Unfortunately, no PWRs in Japan have applied oxygen addition in the feed water yet.

5. Major targets of water chemistry research committee

Through its 24 years of activities the Water Chemistry Research Committee of AESJ has contributed to development of the basic technologies of water chemistry, to enhancement of technical transfer and to promotion of technical bases sharing among all chemists and engineers. The committee is expected to carry out many more activities in the future.

5.1 Technical transfer from experts to the young generation

Trend of number of AESJ members and personnel related to water chemistry are shown in Fig. 7. The total number of the members of AESJ has peaked and then decreased as a result of the shrinking market of nuclear industries. The number of student members has also decreased as the numbers of the members of the water chemistry committee and of personnel doing work related to water chemistry in plant utilities and manufacturers. Decreasing numbers of working chemists and engineers as well as rapid changes in the age of workers have enhanced the need for effective technical transfer. Some parts of water chemistry depend on empirical knowledge bases, which are going to shrink with the retirement of experts. The committee has compiled many data and knowledge bases as a water chemistry handbook [5] and is now arranging them as detailed water chemistry guide books and operating standards. Furthermore, effective technical transfer as well as further improvement in water chemistry may lead to flexible water chemistry control for much safer and more reliable plant operation.

5.2 Technological innovation

There is no end for technical development. Even if some problem is avoided by applying countermeasures, new events will often appear to cause another problem. Water chemistry is often recognized as a typical problem solving type technology, which can forecast future problems or detect small anomalous conditions which could be symptoms for future trouble at a very early stage, and then to contribute to preparation of suitable countermeasures before the trouble extends to a serious incident. For R&D projects it is essential to find suitable subjects and at the same time secure authorization and financial support. One of the key roles of the Water Chemistry Research Committee is to set up the road map for water chemistry R&D as a result of collaborative discussions between industry, government and academia. As the first stage of the road map, suitable subjects and then suitable approaches and budget plans are proposed.

7. Conclusion

Water chemistry has had important contributions to safe and reliable plant operation of NPPs. Some parts of water chemistry depend on empirical knowledge bases, which are going to be lost as a result of retirement
of experts. The Water Chemistry Research Committee of AESJ has played important roles to enhance improvement in water chemistry control, to share knowledge and experience with water chemistry, to establish common technological bases of plant water chemistry and then to transfer them to young generation. Furthermore, the committee continues to contribute to arranging new challenging R&D proposals for further improvement in water chemistry control through road map planning.

Acknowledgement
The authors wish to express their sincere thanks to members of the research committee on “Water Chemistry Standard” of AESJ for their cooperation in compiling this article.

Abbreviations
AESJ: Atomic Energy Society of Japan  
BWR: boiling water reactor  
ECP: electrochemical corrosion potential  
FPP: fossil power plant  
LWR: light water reactor  
LWR: light water reactor  
MSDR: main steam line dose rate  
NPP: nuclear power plant  
NWC: normal water chemistry  
HWC: hydrogen water chemistry  
IGSCC: intergranular stress corrosion cracking  
JISP: Japanese Improvement and Standardization Program  
PWR: pressurized water reactor  
PWSCC: primary water stress corrosion cracking  
TGSCC: transgranular stress corrosion cracking

References

Shunsuke Uchida
BS, Physics, Osaka University (1964), PhD, Nuclear Engineering, University of Tokyo (1979)
He was a professor at Tohoku University for 6 years after completely a 35-year long career in water chemistry research at Hitachi, Ltd. Currently, he serves as the vice chair of the Water Chemistry Standard Committee.