Zinc injection into the reactor coolant of Pressurized Water Reactor (PWR) is one of the most effective techniques for removing radioactive cobalt from the chromite type spinel oxides in the inner layer of reactor coolant component surfaces. Many documents have reported that zinc injection applied plants have generally achieved positive dose rate reduction effects for the reactor coolant components and piping.

Tsuruga Nuclear Power Plant unit 2 (hereafter Tsuruga unit 2) which applied zinc injection in 2005 has also achieved good dose reduction effects in most primary coolant piping. However, some piping without dose-rate reduction effects exist, it has come to an issue to plan radiation exposure reduction measures for the works around relevant piping. To plan a reasonable dose-rate reduction measures for respective components and piping in primary systems, it is considered necessary to understand the dose-rate reduction effects of zinc injection mechanically. Therefore, the surface oxides/deposits on piping and fuel cladding tubes with operational histories under zinc injection were investigated.

As a result of the investigation, the changes in specific aspects of oxide layers and CRUDs are found as follow:
- Owing to long-term zinc injection, deposits and oxides on the primary coolant piping are extremely reduced, the boundary between the outer oxide layer and the inner oxide layer become unclear with the thinning of the outer oxide layers.
- At a Pressurizer Spray Piping, the dose-rate increases than before zinc injection. The oxide layers have the same 3-layer construction as before zinc injection, and the surface concentration of the radioactive cobalt is high.
- At the fuel cladding tube surfaces, what is observed is the amount of metal nickel decrease and the chromium composition increase in the spinel type oxide

From these results, it is suggested that, the oxide layers composed principally of zinc chromite spinel grow up on the pipe surface with zinc injection, nevertheless the oxide film on the Pressurizer Spray Piping is similar oxide layers before zinc injection because the zinc feed rate is insufficient at this piping. Therefore zinc injection has effect on the reduction in cobalt uptake by the oxide layers, however such effects can not be achieved the piping where the zinc feed rate is insufficient. And it is suggested that, on the piping surface with zinc injection, the oxide layers are composed of the chromite type spinel oxides, and that what is fallen away and flaked down from the oxide layers deposits on the fuel cladding tube surfaces.

The investigation results obtained this time for the oxide layers and the fuel cladding tube deposits are reflected to our CRUD Evaluation Code, and the Code is optimized. The evaluation results of radiation source obtained from this optimization and the actual data concerning the radiation source behaviour of Tsuruga unit 2 are in good consistency, therefore, the evaluation is confirmed to have sufficient practicality effective for evaluating radiation source after the zinc injection. The radiation exposure evaluation with high-accuracy will become available anytime soon.

Using this modified Code, the evaluation results of dose-rate reduction effects of the zinc injection with a cumulative 34 months at Tsuruga unit 2 shows 32% reduction, compared to the evaluation value for the case without zinc injection.
1. INTRODUCTION

1.1. OUTLINE OF TSURUGA-2 ZINC INJECTION

Tsuruga unit 2 nuclear power plant (4-loop PWR, 1160 MWe) has been operated by the Japan Atomic Power Co. from 1987. Tsuruga unit 2 has Alloy 600 tube steam generators, and commenced Zinc injection at cycle 15 in August 2005, for 4 cycles with a cumulative 34 months as of May 2011, as is shown in table-1.

<table>
<thead>
<tr>
<th>Cycle No.</th>
<th>Start</th>
<th>End</th>
<th>Duration (Months)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>10 Aug, 2005</td>
<td>30 Apr, 2006</td>
<td>8.5</td>
</tr>
<tr>
<td>16</td>
<td>14 May, 2007</td>
<td>23 Aug, 2007</td>
<td>3</td>
</tr>
<tr>
<td>17</td>
<td>14 Mar, 2009</td>
<td>17 Feb, 2010</td>
<td>11</td>
</tr>
<tr>
<td>18</td>
<td>12 Jul, 2010</td>
<td>07 May, 2011</td>
<td>10</td>
</tr>
</tbody>
</table>

Tsuruga unit 2 injects depleted zinc (Zn64<99%) into the primary coolant in the Reactor Coolant System (RCS) via the sample system return line back into the Volume Control Tank (VCT) in the Chemical and Volume Control System (CVCS) with a zinc injection device. The target concentration of zinc was 5ppb for most of the cycles and was controlled successfully within 5 to 7 ppb except at the beginning of zinc injection start.

1.2. OBJECTIVE

There have been several investigations of the zinc injection effects on the dose-rate reduction. At Tsuruga unit 2, a significant benefit with regard to reduction of dose-rate has been observed as described below. However the degree of the zinc injection effects on the dose-rate reduction depends on the locations and the material of the plant-specific primary coolant system components. It is therefore necessary to develop the evaluation method for dose-rate reduction from primary system with high precision considering the plant characteristics of Tsuruga unit 2.

Meanwhile, some improvements of the primary coolant chemistry control in PWRs include the optimization of dissolved hydrogen (DH) control to maintain the soundness of the component and piping materials, and the modification of pH control to reduce the dose-rate.

At Tsuruga unit 2, the followings are considered (1) the optimization of DH control – DH reduction in steps; 25 cm³/kg-H₂O which is current value, 15 cm³/kg-H₂O and 5 cm³/kg-H₂O – based on the PWSCC experiments, etc., and (2) the modification of pH control - changing the lithium control method from the current modified lithium control to the constant pH control. If these improved controls of coolant chemistry are applied, it would greatly influence the RCS environment. Therefore, it is required to evaluate the effects of these improved chemical controls together with the zinc injection on the radiation source behaviors, and to take appropriate actions based on those evaluation results.

In order to establish an appropriate prediction method for dose-rate, it is considered essential to understand the CRUD transfer in the primary coolant loop including the interface between fuel cladding on which radioactive corrosion products are generated and primary coolant. It was expected that the characteristics of the CRUD – metal and radionuclides - deposited on the fuel cladding and the primary piping would be changed especially due to zinc injection started from the cycle 15. Therefore to evaluate the behavior of the radionuclide in the primary coolant, an investigation was performed for the oxide layer of the primary coolant piping and the CRUD scraped from both the fuel cladding and the primary coolant piping which were sampled in the refueling outage (RFO) 17.

2. DATABASE OF WATER QUANTITY & DOSE-RATE

2.1. PRIMARY COOLANT CONTROL

In the case of Tsuruga unit 2, RCS boron concentration starts at 1400 ppm and ends at 100 ppm during a plant operation cycle by the dilution of RCS. The RCS pH value is controlled within 6.8 to 7.4 at 285 degrees Celsius based on the Modified-Li-Control method, limiting the RCS lithium concentration not to exceed 3.5 ppm.
RCS dissolved oxygen is always maintained below 5 ppb, by keeping the RCS dissolved hydrogen constant within 25-27 cm³/kg-H₂O.

The zinc injection in Tsuruga unit 2 has been carried out since the cycle 15 in 2005 without changing the water chemistry control method.

2.2. RADIOCHEMISTRY RESPONSE TO ZINC INJECTION

Soluble radioactive cobalt with its particle size below 0.45 μm in primary coolant increases immediately after zinc injection. ⁶⁵⁸Co and ⁶⁰⁰Co concentration during zinc injection have the maximum value at around 5 Bq/cm³ and 50 Bq/cm³ respectively, and they are 5-20 times as much as those before injection. Although the insoluble radioactive cobalt concentration does not have a sharp response to the zinc injection, it gradually increases with the zinc injection throughout an operation cycle, and it comes to be about 10 times at the end of a cycle compared to that of at the beginning of a cycle.

2.3. DOSE-RATE RESPONSE TO ZINC INJECTION

The dose-rate trends in the primary system components of Tsuruga unit 2 are shown in table-2. The dose-rates at Steam Generator (SG) channel head (Cold), the crossover leg and the CVCS regenerative heat exchanger, have shown remarkable reduction trends. The dose-rate reduction effects in these locations are about 55%. The dose-rate reductions of 32%-47% at the hot leg and the cold leg respectively, are observed. The dose-rate at the Pressurizer Spray Piping, however, is increased of 240%, because RCS including zinc can not be supplied to the pressurizer during plant operation. The dose-rate reduction effect in the hot leg does not continue excluding the first zinc chemistry cycle. It is believed that the trends of those are caused by influence of the surrounding dose-rate environment and not slowing in the zinc effect.

<table>
<thead>
<tr>
<th>Survey Locations</th>
<th>Dose-rate (mSv/h)</th>
<th>Reduction Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>No Zn</td>
<td>After Zn</td>
</tr>
<tr>
<td>Hot Leg</td>
<td>0.22</td>
<td>0.16</td>
</tr>
<tr>
<td>Crossover Leg</td>
<td>0.39</td>
<td>0.27</td>
</tr>
<tr>
<td>Cold Leg</td>
<td>0.64</td>
<td>0.51</td>
</tr>
<tr>
<td>SG Channel Head (Hot)</td>
<td>46</td>
<td>36</td>
</tr>
<tr>
<td>SG Channel Head (Cold)</td>
<td>94</td>
<td>60</td>
</tr>
<tr>
<td>Pressurizer Spray Piping</td>
<td>0.5</td>
<td>0.7</td>
</tr>
<tr>
<td>CVCS Regenerative Heat Exchanger</td>
<td>3.3</td>
<td>1.0</td>
</tr>
</tbody>
</table>

3. EXAMINATION

3.1. SAMPLES

Some samples were taken from the Pressurizer Spray Piping and the CVCS Letdown Piping to have been replaced at 17th RFO, for investigating the specific aspects of the loose CRUD and the surface oxide layers grown up under the zinc injection environment. Since the primary coolant flow-rate in the Pressurizer Spray Piping is less than 1 m³/h during plant operation, the zinc injection effect is rather small. On the other hand, the CVCS Letdown Piping is adjacent to the Crossover Leg (CO/L) of the primary system main coolant piping, so the water chemistry and the zinc injection history are equivalent to CO/L.

Also some samples were taken from the deposited CRUD on fuel cladding of spent fuel removed at 17th RFO. The CRUD scraped by special equipment from span 1, 3, 5, 7 and 8 as shown in Figure 1. Figure 1 shows the sampled pipes and the sampling positions of the CRUD deposited on the fuel. The outlines of sample pipes are shown in Table 3, and the outlines of fuel assemblies are shown in Table 4. The appearances of the pipes and the CRUD deposited on the fuel cladding are shown in Figure 2.
Table 3 The outline of sampled pipes

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature</th>
<th>Flow-rate</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressurizer Spray Piping</td>
<td>270 degrees Celsius</td>
<td>~1 m³/h</td>
<td>The exposure to zinc is small.</td>
</tr>
<tr>
<td>CVCS Letdown Piping</td>
<td>258~278 degrees Celsius</td>
<td>28.6 m³/h</td>
<td>The exposure to zinc is big.</td>
</tr>
</tbody>
</table>

Table 4 The outline of fuel assemblies

<table>
<thead>
<tr>
<th>Removed RFO</th>
<th>Burned cycle</th>
<th>Total burn-up</th>
</tr>
</thead>
<tbody>
<tr>
<td>17ᵗʰ</td>
<td>3</td>
<td>46,358 MWD/t</td>
</tr>
<tr>
<td>15ᵗʰ</td>
<td>3</td>
<td>46,365 MWD/t</td>
</tr>
<tr>
<td>7ᵗʰ</td>
<td>3</td>
<td>47,598 MWD/t</td>
</tr>
</tbody>
</table>

3.2. ANALYSIS

The inner surfaces of pipe-samples were analyzed by Scanning Electron Microscope/Energy Dispersive X-ray Spectroscopy (SEM/EDS). The surface CRUD and oxide layers on the pipes were recovered by separating into the loose CRUD, the outer oxide layer, and the inner oxide layer using the step peel-off method shown below. Then, the chemistry and the radioactive elements of each of the separated samples were analyzed. By comparing with the results of analysis for loose CRUD layer, outer oxide layer and inner oxide layer on the surfaces of Pressurizer Spray Pipe and CVCS Letdown Pipe, an evaluation of the effect of the zinc injection on the oxide layer aspects was performed.

- Loose CRUD: Ultrasonic treatment The loose CRUD was separated from sample by Ultrasonic sound at the first.
- Outer Oxide: Cathodic electrolysis
  The outer oxide layer was dissolved and separated from sample by reductive dissolution, by using the sample as cathode and the platinum as anode, after Ultra-sonic treatment.

- Inner Oxide: Anodic electrolysis
  The inner oxide layer was dissolved and separated from sample by oxidizing dissolution, by using the sample as anode and the platinum as cathode, after Cathodic electrolysis.

The CRUD deposited on the surface of the fuel was analyzed by SEM/EDS, chemical analysis, and radioactive measurement, and an evaluation of the effect of the zinc injection on the CRUD aspects deposited on fuel was performed.

4. RESULTS

4.1. OXIDE-LAYER AND CRUD ON PRIMARY SYSTEM PIPING

The results of the calculated masses of the oxide on each of the oxide layers from the chemical analysis results for recovered samples by separating treatment are shown in Figure 3. Also, the results of the calculated surface concentrations of the radioactive cobalt on each of the oxide layers are shown in Figure 3. The outline is as follows:

- At Pressurizer Spray Pipe, 90% of the oxide is in the inner oxide layer.
- At CVCS Letdown Pipe, 50% of the oxide is in the outer oxide layer, and another 50% is in the inner oxide layer, and the ratio of the outer oxide layer is higher than that of the Pressurizer Spray Pipe.
- At CVCS Letdown Pipe, the surface concentrations of $^{58}$Co and $^{60}$Co are half or less than those of the Pressurizer Spray Pipe.
- The surface concentration of $^{60}$Co, as compared with $^{58}$Co, is observed to have the tendency that in the inner oxide layer is higher on both Pressurizer Spray Pipe and CVCS Letdown Pipe.
composition of the inner oxide layer is chromium. It is similar to the structures of the oxide layers without the zinc injection. Zinc is mainly distributed in the inner oxide layer.

- Meanwhile at the CVCS Letdown Pipe, the interface boundary between the outer oxide layer and the inner oxide layer is not clear. The outer oxide layer is rich with chromium, and the difference in compositions of the outer oxide layer and the inner oxide layer is small. Zinc is uniformly distributed both in the outer oxide layer and the inner oxide layer.

- At both Pressurizer Spray Pipe and CVCS Letdown Pipe, the chromium concentration at the surface film of the inner oxide layer is relatively high, and the nickel and the zinc concentrations tend to be higher at the same location.

Figure 4  The distributions of radioactive cobalt in the oxide layers

Figure 5  The appearances of cross section by TEM

Figure 6  The depth profile of the oxide layers by TEM/EDS
Figure 7 shows the results of the X-Ray Diffraction (XRD) analysis and the electron distraction analysis on the surfaces of the pipes by TEM. The outline is as follows:

- The spinel type oxides are identified on surface and in the inner oxide layer of cross section of the pipes.

![Figure 7: The results of the crystal structure analysis on the pipes](image)

4.2. CRUD ON FUEL CLADDING

The results of chemical analysis of the recovered deposits from the fuel surface are shown in Figure 8. The results of the same analyses at the 15th RFO of the first outage after starting zinc injection, and the 7th RFO without zinc injection are also shown in Figure 8. The fuel assemblies investigated at the 7th and the 15th RFOs and that investigated at this 17th RFO are equivalent in the fuel cycle numbers and the total burn-ups. The outline is as follows:

- The nickel composition at the 17th RFO shows a lower value than those at the 7th RFOs. The surface concentration of $^{58}$Co shows a similar tendency to nickel.
- Meanwhile, the chromium composition shows a higher value than those at the 15th and the 7th RFOs. The surface concentration of $^{60}$Co also shows a similar tendency to chromium.

![Figure 8: The chemical compositions of CRUDs deposited on the fuels](image)

The results of XRD analysis of the deposits on the fuels at the 7th RFO before the zinc injection and the 17th RFO after the zinc injection are shown in Figure 9. The outline is as follows:

- At the 17th RFO, the spinel type oxides and the zirconium oxides (ZrO$_2$) are identified.
- The metal type nickel identified at the 7th RFO is not identified at the 17th RFO.
5. DISCUSSION

5.1. CORROSION PRODUCT BEHAVIOR IN THE PRIMARY SYSTEMS AFTER ZINC INJECTION

From the analysis results, the aspects of the deposits on the primary system piping are considered as follows:

- At CVCS Letdown Piping, the boundary between the outer oxide layer and the inner oxide layer is not clear after the zinc injection, and the chromium composition in the outer oxide layer is relatively higher. At Pressurizer Spray Piping, on the other hand, the structure of the oxide film is composed of 3 layers which are the same as the structure before the zinc injection\(^1\)\(^2\).
- The surface concentration of the radioactive cobalt at CVCS Letdown Piping is below the half at Pressurizer Spray Piping. However, the radioactive cobalt composition in the outer oxide layer is higher than at Pressurizer Spray Piping.
- Before the zinc injection, the inner oxide layer is composed of the regular-spinel type oxides mainly containing chromium, and the outer oxide layer is composed of the inverse-spinel type oxides mainly containing iron. So the layer structure is clear owing to the clear difference between the states of the crystals\(^3\).
- By the zinc injection, zinc is positioned in the tetrahedron structure of the regular-spinel type oxide, and the regular-spinel type oxide is transformed into the thermodynamically stable zinc-chromite (Zn\(_2\)Cr\(_2\)O\(_4\)) \(^4\)\(^5\)\(^6\).
- Along with this zinc-chromite formation, the chromium diffusion from the inner oxide layer into the outer oxide layer is constrained, the solubility of the outer oxide layer (inverse-spinel type oxide) increases, and the outer oxide layer dissolves and vanishes \(^7\). As a result, the inner oxide layer is exposed onto the surface.
- Meanwhile, in the regular-spinel type oxide in the inner oxide layer, because of the high iron diffusion rate in the oxide \(^8\)\(^9\), the concentration of iron becomes high in the surface area, and the solubility increases compared to the inside of the layer, to lose its robustness. This regular-spinel type oxide without the robustness comes to be the new outer oxide layer.
- Cobalt is positioned in the tetrahedron structure of the regular-spinel type oxide in the same way as zinc. At CVCS Letdown Piping, chromium in the outer oxide layer exists as the chromite form of the regular-spinel type oxide, therefore, the cobalt comes to be also contained much in the outer oxide layer.
- Also, since the potential energy of zinc for the tetrahedron structure of the regular-spinel type oxide is higher than that of cobalt, the cobalt inventory in the oxide layer decreases by the zinc injection.
- On the other hand, Pressurizer Spray Piping has a small flow rate, and the zinc supply is insufficient. Therefore, the effect of the zinc injection is small, and the oxide layer is considered to have shown the conventional structure.

For the aspects of the CRUDs deposited on the fuel after the zinc injection are considered as follows:

- The surface concentrations of iron and nickel are decreased after the zinc injection. Also the nickel/iron ratio is decreased.
- Meanwhile, the surface concentration of chromium is increased after the zinc injection. Also the zinc concentration is increased.
- The inner oxide layer made of the zinc-chromite formed by the zinc injection excels in robustness, and has corrosion suppression effect. So the dissolution rates of iron and nickel from the primary coolant piping are decreased. Especially, owing to the corrosion suppression effect in the S/G tubes, the migration mass of nickel into the core is decreased.
- As is shown above, the surface film of the inner oxide layer formulated after the zinc injection is an oxide rich with iron and chromium, and it is easily fallen away and flaked down, to deposit on the fuel surface. So the chromium concentration in the fuel deposit is increase because of the high concentration of chromium in the inner oxide layer.

- Figure 10 shows the comparison between the chemical compositions of the respective oxide layers at the primary coolant piping and those of the CRUDs on the fuel. The chemical compositions are similar between the outer oxide layer and the CRUD deposited on the fuel. The ratio of the bivalent elements (Ni and Zn) to the trivalent elements (Fe and Cr), (Ni+Zn)/(Fe+Cr), is about 0.5. And with the result of XRD showing of the spinel type oxide peak, it is indicated that the spinel type oxide is formulated.

- These results support the hypothesis that those fallen away and flaked down from the inner oxide layer of the surface of the primary coolant piping as described above, deposit on the fuel.

- Figure 11 schematically shows the behavior of CRUDs in the primary coolant system in PWR with the zinc injection.

![Figure 10](image1.png)

**Figure 10** Top: the chemical compositions of the oxide layers on CVCS Letdown Pipe
Bottom: the chemical composition of the CRUD deposited on the fuel

![Figure 11](image2.png)

**Figure 11** The behavior of the corrosion products in the primary system in PWR with zinc injection
5.2. THE EVALUATION OF THE RADIATION SOURCE INVENTORY (ACE-II CODE)

An evaluation using a computer code is performed to investigate and assess the inventories of radioactive elements in the primary coolant system for the future study of reducing radioactive-exposure at Tsuruga unit 2. The used code is named Activated CRUD Evaluation Code version 2 (ACE-II Code), and ACE-II is developed for evaluating the CRUD behavior of in the primary coolant system of PWR\textsuperscript{10}. The primary coolant system is separated into 19 segments in the code, to evaluate the transfer-behavior of the metal elements and radioactive elements in the materials and the primary coolant, as shown in Figure 12. The parameters in the respective segments use documented or theoretical values, though, by using the actual plant data, it is possible to optimize the code with the plant-specific characteristics. This time, in order to improve the evaluation accuracy, the parameters are optimized concerning the deposition and erosion behaviors of the CRUDs deposited, and the dissolution and erosion behaviors of the outer oxide layers shown in Figure 12. Based on the investigation results of the deposits on the fuel and the primary system piping surfaces, Figure 13 shows the comparison between the evaluation results before and after the improvement and the actual data of Tsuruga unit 2. The outline is as follows:

- By the optimization, the evaluation values and the actual values are in good consistency.
- From the evaluation results, the ACE-II evaluation is confirmed to have sufficient practicality effective for predictively evaluating the trend of dose-rates after the zinc injection.
- By a similar evaluation, it is evaluated that the effect of the zinc injection for reducing dose-rates is a 32% reduction at the 17\textsuperscript{th} cycle as compared to the case without the zinc injection.

5.3. THE EVALUATION OF RADIATION SOURCE INVENTORY IN THE FUTURE

Using the optimized ACE-II, a predictive evaluation of the dose-rates until 22\textsuperscript{nd} cycle with the same water chemistry and the zinc injection continued is performed. In addition, as a future dose-rate reduction measures, a predictive evaluation of the dose-rates for a case with a low DH (15 cm\textsuperscript{3}/kg-H\textsubscript{2}O) control and constant pH (pH = 7.3 at 285 degrees Celsius) control is performed. Figure 14 shows the results. The outline is as follows:

- By the long term evaluation, the radiation source inventory shows a reduction tendency over time by the zinc injection. As the result, the dose-rate in SG channel head at the 22\textsuperscript{nd} RFO is evaluated to be about 9% less than that at the 18\textsuperscript{th} RFO actual data.
- With a constant pH control, the dose-rate in SG channel head at the 22\textsuperscript{nd} RFO is evaluated to be about 7% less than without the constant pH control. With a low DH control, the dose-rate in SG channel head at the 22\textsuperscript{nd} RFO is evaluated to be about 8% less than without the low DH control.
- With a low DH control + a constant pH control, the dose-rate in SG channel head at the 22\textsuperscript{nd} RFO is evaluated to be about 17% less than without both of the controls.
- In conclusion, it is evaluated that the radioactive cobalt inventory in the primary coolant system continuously decreases by the long term zinc injection. And some dose-rate reduction effect is evaluated to be expected by applying a low DH control and a constant pH control.
At Tsuruga unit 2 at the 17th RFO after the third zinc injection, the investigations of the depositions on the primary coolant piping and the fuel was performed. The results are as follows:

- The Ni inventory in the primary coolant system is decreased because the diffusion of metal element into the primary coolant is constrained by the zinc-chromite formation in the oxide layer on the surface of the primary coolant piping.
- The difference in the compositions of the outer oxide layer and the inner oxide layer of the oxide layers on the primary coolant piping surfaces become small because the chromium composition increases in the outer oxide layer by the long term zinc injection.
- As the result, the nickel metal decrease and the chromite type spinel oxides deposit on the fuel, which is thought to be separated from the outer oxide layer on the primary coolant piping, are observed.
- As the result of reflecting the insights for the behavior of the radioactive element transfer with the long term zinc injection into the Activated CRUD Evaluation Code (ACE-II), it is confirmed that the radiation source behavior prediction at Tsuruga unit 2 can be precisely performed, by benchmark with the actual data.
- Using this code, with the prediction of the dose-rate reduction effect with the zinc injection at Tsuruga unit 2 in the future, the dose-rate reduction effect with the enhanced water chemistry in the future is predictively evaluated. As the result, it is confirmed that some dose-rate reduction effect is expected by applying low DH control and constant pH control.

7. REFERENCES

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Study on a Corrosion Products Behavior with Zinc Injection in PWR Primary Circuit Based on the CRUD Investigation in Actual Plant

September 25, 2012

Kenji HISAMUNE
THE JAPAN ATOMIC POWER COMPANY
MITSUBISHI HEAVY INDUSTRIES, LTD
NUCLEAR DEVELOPMENT CORPORATION
TSURUGA Nuclear Power Plant unit 2

◆ ELECTRIC OUTPUT : 1,160,000 KW
◆ REACTOR TYPE : Pressurized water reactor (PWR)
◆ FUEL : Low enriched uranium (approx. 89 tons)
◆ COMMERCIAL OPERATION START : Feb. 17, 1987
◆ STEAM GENERATOR MATERIAL : Alloy 600 TT (4 Loops)
Presentation Outline

◆ Background
◆ Objectives
◆ Analysis of Primary Piping
◆ Analysis of Fuel CRUD
◆ Corrosion Products behavior
◆ Evaluation of Dose-rate
◆ Conclusion
Background

1. Tsuruga NPP unit 2 commenced zinc injection at cycle 15\textsuperscript{th} in Aug. 2005, for 4 cycles with cumulative 34 months as of May 2011.

2. The degree of zinc injection effects on the dose-rate reduction depends on the location.

<table>
<thead>
<tr>
<th>Survey Locations</th>
<th>Dose-rate (mSv/h)</th>
<th>Reduction Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>No Zn</td>
<td>After Zn</td>
</tr>
<tr>
<td></td>
<td>14\textsuperscript{th} RFO</td>
<td>15\textsuperscript{th} RFO</td>
</tr>
<tr>
<td>Hot Leg</td>
<td>0.22</td>
<td>0.16</td>
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<tr>
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<tr>
<td>Cold Leg</td>
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<tr>
<td>CVCS Regenerative Heat Exchanger</td>
<td>3.3</td>
<td>1.0</td>
</tr>
</tbody>
</table>
Objectives

1. To clarify the characteristics of the oxide layer on piping with or without zinc exposure.

2. To discuss a corrosion products behavior in RCS, based on the analysis data concerning the CRUD and oxide layer on both the piping and the fuel cladding.

3. To optimize the radiation exposure evaluation code for high-precision evaluation

4. To evaluate the dose-rate tendency in the case of continuing zinc injection and applying chemical control changes by using optimized code.
Preparation of the Sample from the Oxide Layer on the Primary Piping

<table>
<thead>
<tr>
<th>Location</th>
<th>Pressurizer (PRZ) Spray Piping</th>
<th>CVCS Letdown Piping</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>270 °C</td>
<td>258-278 °C</td>
</tr>
<tr>
<td>RCS Flow Velocity</td>
<td>Less than 1 m³/h</td>
<td>28.6 m³/h</td>
</tr>
<tr>
<td></td>
<td>Zinc supply: insufficiency</td>
<td>Zinc supply: sufficiency</td>
</tr>
<tr>
<td>Dose-rate reduction</td>
<td>240%</td>
<td>54% at Crossover leg</td>
</tr>
</tbody>
</table>

Surface oxide layers were divided into 3 layers:

- Loose CRUD
- Outer Oxide
- Inner Oxide

Pre-treatment for the oxide layers
Comparison of the Oxides including Radioactive Cobalt between PRZ and CVCS

Oxide Layer
- PRZ: Inner >> Outer >> Loose CRUD (as Pre-Zn injection)
- CVCS: Inner ≈ Outer >> Loose CRUD

Radioactive Co
- PRZ >> CVCS
Analysis of Primary Piping 3

Oxide Layer Depth Profiles of PRZ and CVCS Piping

**Interface Boundary (Inner Layer / Outer layer)**

- **PRZ**: Not clear (as pre-Zn injection)
- **CVCS**: Clear
Crystal Structure Analysis of the Pipe’s oxide Sample

The results of XRD

Crystal Structure
Inner Oxide Layer: Spinel Type Oxide (CVCS and PRZ)
Analysis of Fuel CRUD 1

Preventing Deposit Samples and the Results of Chemical Composition

Before Zn

Scraping from Cladding

0.45 micron Filtration

SCRUD Sample

After Zn

<table>
<thead>
<tr>
<th>Finish using RFO</th>
<th>Burned cycle</th>
<th>Total burn-up</th>
</tr>
</thead>
<tbody>
<tr>
<td>17th</td>
<td>3</td>
<td>46,358 MWD/t</td>
</tr>
<tr>
<td>15th</td>
<td>3</td>
<td>46,365 MWD/t</td>
</tr>
<tr>
<td>7th</td>
<td>3</td>
<td>47,598 MWD/t</td>
</tr>
</tbody>
</table>

Chemical Composition after Zn

Ni : Decrease
Cr : Increase
Crystal Structure Analysis of Deposit samples on Fuel Cladding

Crystal Structure

17th RFO: Spinel Type Oxide (as Zn injection)
7th RFO: Spinel Type Oxide and Ni metal
Comparison of Chemical Compositions between the Pipe’s Oxide and Fuel’s CRUD

Chemical Composition
Fuel CRUD \equiv Outer Oxide Layer
(Ni + Zn)/(Fe + Cr) \equiv 0.5
Corrosion Products behavior 2

Mechanism of the Corrosion Products behavior in PWR Primary Circuit with Zinc

Spinel type oxide (incl. Cr)
Outer Oxide layer
⇒ Fuel Cladding

Surface of Fuel Cladding
Increase Spinel type Oxide (incl. Cr)

Surface of Oxide Layer
Fe Rich : easy soluble and fallen away

Fe\textsuperscript{2+}
Co-58
Co-60

Decreased loose CRUD
The inner oxides exposed to surface become the new outer oxide layer
Inner oxide layer

Fe\textsuperscript{2+}
Cr,Fe (Ni) O\textsubscript{4}
Chromite Spinel

Ni\textsuperscript{2+}, Fe\textsuperscript{2+}, Cr\textsuperscript{3+}

Base metal
(Surface of piping)
Evaluation of Dose-rate 1

Outline of the MHI Activated CRUD Evaluation Code (ACE-II)

Dose Rate (after optimization of CODE)
Evaluation Value ≈ Actual Value

Zn Injection Effect (Dose Rate Reduction)
17th : 32% (vs Without Zn Injection)
Evaluation of Dose-rate 2

Dose-Rate Prediction for the Future with Continuing Zinc & Chemical Control Changes

Evaluated Dose Rate Reduction (vs 18th RFO)
7% : Constant pH
8% : DH 15 Control
17% : Constant pH + DH 15 Control
Conclusion

1. Owing to long term zinc-injection, the chromium composition increases in oxide layer on piping, and interface boundary between the outer and inner oxide layer becomes unclear compare to without zinc-injection.

2. The Ni inventory in the RCS is decreased cause formation of the zinc-chromite on the primary components constrain diffusion of metal elements.

3. Scheme of the CRUD behavior was estimated by utilizing the ACE-II improved in the basis of the results from the CRUD investigation in actual plant.

4. Using the improved ACE-II, prediction of the dose-rate reduction effects in the future are confirmed with applying the water chemistry modification.