Fate of Radionuclides in the Light Water Moderator of a Research Reactor

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The fate of radionuclides produced in a light water moderator was investigated by assaying with a Ge(Li) detector sampled coolant water and the waste water produced by regeneration of resins, measuring the radiation dose rates along the surface of the resin column length with TLDs, and studying the sorption of radionuclides to resins in dynamic experiments. The build up concentrations of short-lived radionuclides, produced by activation in the reactor core water and the amounts of radionuclides sorbed on the resin bed, as estimated from a compartment model, are reported. A method for estimating the production rate of soluble radionuclides with long half-lives in the core water has been developed. Changes in the radiation dose rates along the resin column length recorded during reactor operation and after shut-down, showed that the sorbed radionuclides did not migrate downward, as expected from the chromatography theory, rather they were decreased by the decay process. Moreover, the slopes of the dose rates on both sides of the resin surface were almost identical. These results show the behavior and distribution of radionuclides in the light water moderator of a research reactor.

KEYWORDS: resin bed, purification circuit, distribution, radionuclides, light water moderator, primary coolant water, sorption, column, dose rates, activation process, thermoluminescence dosemeters, concentration ratio

I. INTRODUCTION

Radioactivity buildup around the reactor core, especially in the primary coolant systems of the purification circuit of water reactors, is cumbrous because it increases the exposure of personnel during tasks involved in reactor shut-down and/or start-up. To reduce the radiological burden, we need to better understand the behavior of the radionuclides released from component materials such as aluminum and/or materials produced from impurities in the coolant water by the activation process.

The Kyoto University Research Reactor (KURR) in Osaka Prefecture, Japan is a light water-moderated reactor utilizing 90% enriched uranium fuel in an aluminum tank 2 m in diameter and about 7 m deep. Deionized light water of about 3.0×10¹ m³ serves as a neutron moderator as well as the primary coolant and shielding material. The KURR initially was operated at 1 MWth (hereafter, MW) in 1964(1), and its power was raised to 5 MW in 1968. Operation of the KURR for 70~80 h a week, Tuesday through Friday, for more than two decades, a thermal output of about 1×10¹ GWh yearly(2). Part of the primary coolant water circulated through the cooling system is forced to flow into an ionexchange resin bed, the major purification system used to reduce the radionuclide contents of the water.

We examined the fate of radionuclides in the primary coolant water and in the resin column placed in the purification circuit during the periods when the reactor was in operation and shut down by making a radiometric assay of coolant water samples and by monitoring the radiation field intensity along the length of the column with thermoluminescence dose-
meters (TLDs). No in situ experiments during power operation had been made previously because of the high radiation field. Dynamic experiments for radionuclides in the coolant water, especially $^{24}$Na, were done to examine their sorption with the resins.

II. PRIMARY COOLANT PURIFICATION CIRCUIT

The KURR primary coolant system originally was designed to handle a flow of $2.4 \times 10^8$ m$^3$/h at 1 MW$^{(1)}$. The flow was raised to about $9.0 \times 10^8$ m$^3$/h in 1968 for reactor operation at 5 MW. The primary coolant purification circuit (PCPC) consists mainly of two rows of 12 cartridge filters each, one row located upstream and one downstream of two ionexchange resin columns. As shown in Fig. 1, coolant water pumped from about a depth of 4 m in the reactor core tank flows into the PCPC then passes down through the resin column at a flow rate of about $1.0 \times 10^1$ m$^3$/h before returning to the water surface of the core tank. All the equipment is housed in the basement of the reactor containment building together with the heat exchange apparatus of the secondary coolant system.

The disposable cartridge filter (Cuno microcreen III) used is made of cellulose-melamine fiber that filters suspended particulate matter such as crud$^{(2)}$ with a nominal size greater than 5 $\mu$m. The resin column used for the PCPC is stainless steel into which commercially available anion-cation mixed resins are slurried to make a bed about 140 cm long. The cation exchanger in hydrogen form, 105 dm$^3$, grain diameter $0.65 \pm 0.05$ mm, is mixed with the anion exchanger in hydroxide form, 230 dm$^3$, diameter of $0.57 \pm 0.05$ mm, in the column (55 cm inner dia., 210 cm long). The respective particle densities of the cation and anion exchangers are 1.23 and 1.06 g/cm$^3$. The fluid flow can be switched to another column, when the specific conductivity in the effluent from the column shows a tendency to increase. In the four years since 1989, the fluid flow has been switched six times in order to renew or regenerate the resins. The PCPC has been maintained at an apparent pH in the range of 6.3 to 6.5. Some short-lived radionuclides were found in the coolant water with an Nal(Tl) detector during reactor operation at 1 MW$^{(1)}$.

III. EXPERIMENTS

1. Radiometric Assay of Primary Coolant Water

To assay the radionuclides produced by the activation process, we collected coolant water samples in 250 cm$^3$ teflon vessels from valves upstream and downstream of the column over a 77 h period of reactor operation and a subsequent 87 h after power shut-down. The power reached 5 MW at 11:55 a.m. on September 3, 1991 and was shut down at 17:00 p.m. on September 6, 1991 as was the accompanying operation of the heat exchange circuit. In contrast, the PCPC was operated continuously for 164 h. This means that the water volume that passed through the resin column decreased from $3.0 \times 10^8$ m$^3$, the entire volume in the coolant system, to about $2.2 \times 10^8$ m$^3$, the approximated volume in the core tank excluding the coolant circuit after termination of the heat exchange process. The radiometric assay was done with a Ge(Li) detector on water samples.
whose volumes and measuring times ranged from 10 to 240 cm$^3$ and 600 to 10,000 s, depending on the radioactivity sampled in vessels. The identical geometry for samples was made by adjusting the volume of sampled water to 240 cm$^3$ with deionized water. Correction for differences was made by weighing the samples.

2. Contact Dose Rates along Resin Column Length

To better understand how radionuclides behave in the PCPC, we need to know the radiation levels with time along the resin column length, but recorded data have not been available because of expected high radiation levels around the column. Measurements of the radiation field were made as follows once or twice a day during the period in which the radiometric assay of coolant water was made: A wooden pole, 2 m long, holding 10 to 14 thermoluminescence dosemeters (TLD; 200S, CaSO$_4$ type) positioned 5 to 20 cm apart was attached to the surface of the resin column for 10 to 60 min depending upon the radiation level at the time. After its removal, counting and annealing were done. This method markedly reduced the exposure dose to personnel who made the repeated measurements of the radiation field and gave more reliable results than measurement with a survey meter because the TLDs could be set in the same position each time.

3. Dynamic Studies of Radionuclide Uptake from Sampled Coolant Water

The dynamic sorption method was used to assess radionuclide sorption to mixed resins. A simplified diagram of the experimental set-up is shown in Fig. 2. The solution taken from the valve upstream of the column on October 31, 1991 in the PCPC was placed in a 0.3 dm$^3$ teflon flask. A peristaltic pump forced the 0.243 dm$^3$ fluid through a small column (2.2 cm dia., 2.7 cm long) at the flow rate of 1.07 dm$^3$/h. The mixture of resins, 7.08 g (10.2 cm$^3$ in the solution) was placed on a glass wool filter in the small column. The flask receiving the effluent from the column was detached at intervals from the circulation line and given a radiometric assay with a Ge(Li) detector for 10 to 60 s, depending on the activity present over a 150 min circulation period.

![Fig. 2 Apparatus for dynamic method sorption experiment](image)

IV. RESULTS AND DISCUSSION

1. Characteristics of Radionuclide Buildup in Primary Coolant Water

Changes in the concentration of radionuclides in just the solution flowing into the resin column are shown in Fig. 3 because no major radionuclides except $^{41}$Ar, an inert gas, were detected in the effluent from the column. The concentrations of short-lived radionuclides in the influent (the coolant water from the core tank) soon reached a steady state; the average values at equilibrium being $8.5 \times 10^{2}$ Bq/cm$^3$ for $^{27}$Mg (half-life: 9.5 min, major energy of emitted $\gamma$-rays: 0.843 MeV); $5.3 \times 10^{2}$ Bq/cm$^3$ for $^{24}$Na (15 h, 1.36 MeV); and $6.6 \times 10^{2}$ Bq/cm$^3$ for $^{41}$Ar (1.83 h, 1.29 MeV) in the influent and $3.3 \times 10^{2}$ Bq/cm$^3$ ($^{41}$Ar) in the effluent. The ability of the resin column to attenuate the inert gas level probably is because the effect produced by intra-molecular diffusion into micropores of resin particles, is retarded as also has been observed for $^{137}$Cs migration through a sandy soil$^{10}$. Low level radionuclide species of less than about 5 Bq/cm$^3$ of $\gamma$ energy at 0.140 and 0.250 MeV (Fig. 3) were indeterminate but gradually increased in the influents and showed the same pattern as $^{51}$Cr (maximum concentration, $1.2 \times 10^{2}$ Bq/cm$^3$, half-life 27.7 d, 0.32 MeV). These species were completely removed by the resin bed as were the other reactive nuclides. No $^{28}$Al,
which has a short half-life of 2.3 min, could be detected in the influents because it took about 30 min from sampling at the site until measurements were made in the tracer laboratory.

Table 1 Concentrations of radionuclides in KURR core water measured with a low background Ge(Li) detector 15.7 days after reactor shut-down

<table>
<thead>
<tr>
<th>Radionuclide</th>
<th>Half-life</th>
<th>3-ray energy (MeV)</th>
<th>Concentration (Bq/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>131I</td>
<td>8.04 d</td>
<td>0.3645</td>
<td>1.8×10^{-3}</td>
</tr>
<tr>
<td>137Cs</td>
<td>30.0 yr</td>
<td>0.6616</td>
<td>1.2×10^{-4}</td>
</tr>
<tr>
<td>56Co</td>
<td>70.8 d</td>
<td>0.8108</td>
<td>4.8×10^{-4}</td>
</tr>
<tr>
<td>54Mn</td>
<td>312.5 d</td>
<td>0.8348</td>
<td>2.8×10^{-4}</td>
</tr>
<tr>
<td>60Co</td>
<td>5.27 yr</td>
<td>1.3325</td>
<td>4.1×10^{-4}</td>
</tr>
<tr>
<td>149La</td>
<td>40.3 d</td>
<td>1.5962</td>
<td>7.8×10^{-1}</td>
</tr>
</tbody>
</table>

After reactor shut-down, 24Na appears to be the radionuclide of major importance both in the coolant water and the resin bed because the contents of other short-lived radionuclides are decreased by physical decay.

Low level radioactivities of radionuclides with longer half-lives in the core water were measured with a Ge(Li) detector in a lead-shielded container for 3×10⁶ s after being kept for 1.35×10⁶ s. Samples were taken from the top of the reactor pool in a 3.38 dm³ vessel 2 h after power shut-down. The radionuclide concentrations were less than 1 Bq/cm³ (Table 1). The amount of these radionuclides sorbed to the resin column was estimated by measuring the concentrations in the 5 m³ solution produced by regeneration of the Dowex resins. The resin column had been used for about 13 months since mid-May 1992 and was regenerated on August 29, 1993. During the period of use, the thermal output of the KURR was 6,860 MWh. The amounts of radionuclides, corrected for the decay process at the time at which use of the resin column was stopped are listed in Table 2. Concentrations in the solution for regeneration and production rates (Bq/Wh) that are regulated by the thermal output of the KURR are given in Table 2. The production rates per thermal output were converted by those per day calculated by

\[ P = \lambda M / \left(1 - \exp(-\lambda t)\right), \]

where \( P \) is the production rate (Bq/d), \( \lambda \) the decay constant (1/d), and \( M \) the radioactivity (Bq) produced and accumulated in the resins.
Table 2 Concentrations of radionuclides with long half-lives in waste water produced by regeneration of resins

<table>
<thead>
<tr>
<th>Radionuclide</th>
<th>Concentration (Bq/cm²)</th>
<th>Amount (MBq)</th>
<th>Production rate (Bq/Wh)</th>
</tr>
</thead>
<tbody>
<tr>
<td>⁵¹Cr</td>
<td>3.4 x 10⁻⁵</td>
<td>1.1 x 10⁹</td>
<td>1.6 x 10⁻³</td>
</tr>
<tr>
<td>⁶⁰Co</td>
<td>1.4 x 10⁻⁵</td>
<td>7.0 x 10⁶</td>
<td>1.1 x 10⁻⁶</td>
</tr>
<tr>
<td>⁹²Zr</td>
<td>2.4 x 10⁻⁶</td>
<td>5.3 x 10⁻⁶</td>
<td>5.8 x 10⁻⁷</td>
</tr>
<tr>
<td>⁶⁵Zn</td>
<td>5.1 x 10⁻³</td>
<td>5.3 x 10⁻³</td>
<td>3.0 x 10⁻⁵</td>
</tr>
<tr>
<td>⁶⁵Mn</td>
<td>3.5 x 10⁻⁵</td>
<td>2.1 x 10⁻⁵</td>
<td>4.6 x 10⁻⁶</td>
</tr>
<tr>
<td>⁶⁰Co</td>
<td>7.7 x 10⁻⁶</td>
<td>4.7 x 10⁻⁶</td>
<td>1.2 x 10⁻⁴</td>
</tr>
<tr>
<td>⁶⁰Co</td>
<td>1.2 x 10⁻⁵</td>
<td>6.2 x 10⁻⁵</td>
<td>1.7 x 10⁻⁶</td>
</tr>
</tbody>
</table>

over the time t (d) of reactor operation. This equation is derived from the solution of a fundamental equation of the material balance (dM/dt = P – λM) in the PCPC.

Chromium-51, ⁶⁰Co and ⁶⁵Zn are the major radionuclides sorbed to resins used for about a year. The respective production rates of these soluble constituents of the KURR core water were estimated to be about 1.6 x 10⁻⁵, 1.7 x 10⁻⁴ and 1.2 x 10⁻⁴ Bq/Wh.

The contact radiation dose rates on the column surface from these radionuclides with long half-lives, as measured with a survey meter, were less than a few tens of μSv/h even after several years of operation of the resin bed and the decaying out of radionuclides with short half-lives. This value was less than 0.1% of the maximum value for short-lived radionuclides produced during reactor operation, as shown below.

2. Radiation Field Intensity along Resin Column Length

Radiation field intensity along the resin column length during reactor operation for 77 h is shown in Fig. 4. The radiation dose was greatest above a depth of 60 to 70 cm because the resin surface is about 63 cm from the top flange of the column. The plateau value at the very top of the resin bed recorded after 77 h of operation is thought to be due to a γ field counting inaccuracy resulting from the geometry at the top of the bed, not to an actual decrease in the amount sorbed. Small increases in the radiation field between 28 and

77 h of reactor operation indicate that the rate of physical decay for the entire amount sorbed in the bed is in equilibrium with the inflow into the column. At equilibrium, the radiation dose rate near the top of the resin, about 4 x 10⁻¹ Gy/h, is about three orders of magnitude greater than that near the bottom. This radiation field recorded with the TLDs does not, however, appear to be due to γ emitters from radionuclides sorbed on the resin near the TLD sites but to leakage from the top layer of the resin bed. This is because only ⁴¹Ar, an inert gas, was detected in the effluent from the column. No radionuclides were considered to have accumulated in the resin near the bottom. Another reason for the disagreement in the distributions of the radiation dose rate and the concentration of sorbed radionuclides in the column is that the slopes of the radiation dose rates were almost same for the resin layer and the region of the overlying inflow solution above the resin surface. This suggests that the area near the top layer of the sorbent bed contributes to the sorption of radionuclides and that the radiation dose for this area accounts for both sides of the column surface, showing symmetry with the radiation dose along the column length.

In Fig. 5, the radiation field intensity along the column length after reactor shut-down is shown when about 2.2 x 10⁵ m³ coolant water
3. Sorption of $^{24}$Na in Coolant Water to Resins

For the system shown in Fig. 2, the amount of $^{24}$Na sorbed on the resin is

$$\frac{dM}{dt} = qC - kC - \lambda M,$$  \hspace{1cm} (1)

where $M$ is the radioactivity sorbed on the entire resin at time $t$ (kBq), $t$ the elapsed time after circulation (h), $q$ the flow rate of circulation (dm$^3$/h), $k$ the rate constant of the transfer of radioactivity from the small column (dm$^3$/h) to the flask, $\lambda$ the decay constant (1/h), and $C$ the solute concentration at time $t$ (kBq/dm$^3$).

The mass balance in the circulation system at time $t$ gives

$$C_0 V_f \exp(-\lambda t) = C V_f + M,$$  \hspace{1cm} (2)

where $V_f$ is the volume of the circulating solution (dm$^3$) and $C_0$ the initial concentration in the solution in the flask (kBq/dm$^3$). Substituting $M$ in Eq. (2) and its derivative $(dM/\,dt)$ into Eq. (1), the following equation is obtained:

$$\frac{dC}{dt} = \xi C,$$  \hspace{1cm} (3)

where $\xi = q + k$. $\eta = (q - k)/V_f$.

Setting $C = C_0$ at $t = 0$

$$C/C_0 = \exp(-\xi t).$$  \hspace{1cm} (4)

Substituting Eq. (4) in Eq. (2), the average concentration for $^{24}$Na on the resin, $Q(=M/m)$ is

$$Q = C_0 V_f m^{-1} \{1 - \exp(-\eta t)\} \exp(-\lambda t),$$  \hspace{1cm} (5)

where $m$ is the mass of resin as sorbent (g).

With Eq. (4), the sorption parameter, the so-called the concentration ratio ($Q/C$) is

$$Q/C = \{\exp(\eta t) - 1\} V_f m^{-1}.$$  \hspace{1cm} (6)

Equation (6) indicates that the ratio $Q/C$ increases with time, if Eq. (4) is valid and that equilibrium is not reached between the concentration of resin and the solution phases over a given period.

As shown in Fig. 6, the relative concentrations ($C/C_0$) in the dynamic experiment (solid squares) showed an exponential decrease, which
Estimation of Maximum Amount of Reactive Radionuclides Sorbed on Resin Bed

The build-up concentration of the radioactive nuclides was reached quickly in the primary coolant water, and no reactive radionuclides appeared in the effluents. Moreover the amount sorbed on the resin bed seemed to reflect a steady state because increases in the radiation dose rates became small from 28 h after the reactor was put into operation (Fig. 4). Based on the fact of no appearance of reactive radionuclides in the effluents, setting \( k = 0 \) in Eq. (1) gives the following equation assuming the steady state condition (\( C = C_0 \) and \( dM/dt = 0 \) for \( t \to \infty \)):

\[
M_{\infty} = C_0 \lambda^{-1},
\]

where \( M_{\infty} \) is the maximum amount sorbed on the resin bed in the steady state condition. From Eq. (7) the amount of radionuclides sorbed on the resin bed set in the PCPC was estimated to be \( 1.2 \times 10^8 \text{ Bq (3.2 Ci)} \) for \( ^{24}\text{Na} \) (5.3 \( \times 10^5 \text{ Bq/cm}^3 \) at equilibrium) and 2.0 GBq (5.4 \( \times 10^{-2} \text{ Ci} \) for \( ^{27}\text{Mg} \) (8.5 \( \times 10^2 \text{ Bq/cm}^2 \) at equilibrium). Therefore, owing to the difference in the decay constant \( \lambda \), \( ^{24}\text{Na} \) was the radionuclide of major importance on the resin bed, 60-fold \( ^{27}\text{Mg} \) having been sorbed, even though there was a greater concentration of \( ^{27}\text{Mg} \) in the primary coolant water. Consequently, \( ^{24}\text{Na} \) accounted for more than 99% of the radiation field, taking into account both the amount sorbed and the \( \gamma \)-ray energy emitted.

Information about the fate of radionuclides produced in core water will help us not only to model the behavior of radionuclides in the coolant water but to understand the radiological implications of Na(I) monitor readings, which are under investigation.

### V. Conclusion

The fate of radionuclides in the purification circuit of the primary coolant water of the KURR was examined by (1) a radiometric assay of both the sampled coolant water and the waste water produced by regeneration of the resin, done with a Ge(Li) detector; (2) measurements made with TLDs of the radiation dose...
rates along the resin column length; and (3) a study of radionuclide sorption to the resin done in a dynamic experiment. The results obtained are as follows:

1. The build-up concentration of short-lived radionuclides produced by the activation process that reached the steady state in the primary coolant water within a day during power operation at 5 MW were estimated to be $8.5 \times 10^4$ Bq/cm$^3$ for $^{27}$Mg, $5.3 \times 10^4$ Bq/cm$^3$ for $^{24}$Na, and $6.6 \times 10^2$ Bq/cm$^3$ for $^{41}$Ar.

2. Reactive radionuclides were completely removed by the resin bed, and the concentration found for $^{41}$Ar in the influent was halved in the effluent due to the retardation effect caused by intra-particle diffusion during the migration process. A compartment model, in which the steady state was assumed between the inflow and decay rates in the resin bed, showed that the maximum amounts of the major radionuclides sorbed were $1.2 \times 10^2$ GBq for $^{24}$Na and 2.0 GBq for $^{27}$Mg.

3. The method for determining the production rate of radionuclides with long half-lives in the KURR core water was developed and the rates per thermal output were estimated to be $1.6 \times 10^{-3}$, $1.7 \times 10^{-4}$ and $1.2 \times 10^{-4}$ Bq/Wh for the soluble $^{51}$Cr, $^{60}$Co and $^{65}$Zn constituent, respectively.

4. The maximum dose rate, $4 \times 10^{-1}$ Gy/h was found near the resin surface after 77 h of operation at 5 MW, the increase in the rate being gradual after a few days of the power operation.

5. The distribution of the dose rate along the column length after 77 h of operation was almost identical for both sides of the resin surface, indicative of a very narrow resin band of sorption. This band did not move downward as expected according to chromatography theory, but the radiation field has decreased with the same shape of the distribution as it had after reactor shut-down.

6. No equilibrium was reached for the concentrations of $^{64}$Na in the sampled coolant water and the resin in the dynamic sorption experiment, but $6.2 \times 10^4$ cm$^3$/g of the concentration ratio, $Q/C$ was the minimum distribution coefficient.

---REFERENCES---


