The Great East Japan Earthquake occurred on March 11, 2011 caused the severe incident of Fukushima Daiichi Nuclear Power Station. The leakage of radioactive substances has caused radioactive contamination of agricultural products and environment not only in the surrounding area of the plant but also in the extensive region of Tohoku and Kitakanto districts. After the incident, radioactive contamination of drinking water was detected at several water purification plants, and a number of specimens exceeded the provisional criteria of radioactive iodine (Ministry of Health, Labour and Welfare, 2011-1; Tokyo Metropolitan Government, 2011). Radioactive contamination of drinking water is a great concern of local residents because it causes internal radiation exposure and possibly increases the risk of cancer.

Water purifiers are widely used to remove odor or harmful substances such as residual chlorine and trihalomethanes. As regards household water purifiers, quality labeling about the removal capability for 13 substances is legally obligated in Japan. However, radioactive substances are not included in the 13 substances and there is no information whether household water purifiers can remove radioactive substances. On the other hand, zeolite A4 efficiently removed cesium, strontium and barium, but had no effect on iodine and zirconium. Natural zeolite, mordenite, removed cesium with an efficiency as high as zeolite A4, but the removal efficiencies for strontium and barium were far less than those of zeolite A4. Activated carbon had little removal effects on these elements. In case of radioactive contamination of tap water, water purifiers may be available for convenient decontamination of drinking water in the home.

**Key words:** Radioactive contamination, Tap water, Water purifier, Zeolite

---

**ABSTRACT** — The severe incident of Fukushima Daiichi Nuclear Power Station has caused radioactive contamination of environment including drinking water. Radioactive iodine, cesium, strontium, barium and zirconium are hazardous fission products because of the high yield and/or relatively long half-life. In the present study, 4 pot-type water purifiers and several adsorbents were examined for the removal effects on these elements from drinking water. Iodide, iodate, cesium and barium were removed by all water purifiers with efficiencies about 85%, 40%, 75-90% and higher than 85%, respectively. These efficiencies lasted for 200 l, which is near the recommended limits for use of filter cartridges, without decay. Strontium was removed with initial efficiencies from 70% to 100%, but the efficiencies were slightly decreased by use. Zirconium was removed by two models, but hardly removed by the other models. Synthetic zeolite A4 efficiently removed cesium, strontium and barium, but had no effect on iodine and zirconium. Natural zeolite, mordenite, removed cesium with an efficiency as high as zeolite A4, but the removal efficiencies for strontium and barium were far less than those of zeolite A4. Activated carbon had little removal effects on these elements. In case of radioactive contamination of tap water, water purifiers may be available for convenient decontamination of drinking water in the home.

**Key words:** Radioactive contamination, Tap water, Water purifier, Zeolite
half-lives, and the radioactivities released to the atmosphere by this incident are estimated to be $1.6 \times 10^{17}$, $3.3 \times 10^{16}$, $2.1 \times 10^{15}$, $3.2 \times 10^{15}$, $1.7 \times 10^{13}$ Bq, respectively (Ministry of Economy, Trade and Industry, 2011). In the present study, therefore, we evaluated removal efficiencies of household water purifiers and several adsorbents for these elements from drinking water.

**MATERIALS AND METHODS**

**Materials**

Four pot-type water purifiers purchased from four major manufacturers (models A, B, C and D) were tested. The filter media and other specifications are shown in Table 1. Potassium iodide, potassium iodate, cesium chloride, strontium chloride, barium chloride, zirconium chloride (IV), synthetic zeolite A4 (200 mesh) and activated carbon (powder) were purchased from Wako Pure Chemical Industries (Osaka, Japan). Granular natural zeolite, mordenite, obtained from Miyatyu (Miyagi, Japan) was milled and passed through a 0.25 mm sieve to make it powdered. ICP multielement standard was obtained from Merck (Tokyo, Japan). Tap water was used in all experiments except for the preparation of standard solution to conduct experiments under practical conditions.

**Table 1. Specification of water purifiers used**

<table>
<thead>
<tr>
<th>Filter media</th>
<th>Activated carbon</th>
<th>Ceramic</th>
<th>Hollow fiber membrane</th>
<th>Activated carbon</th>
<th>Ion exchanger</th>
</tr>
</thead>
<tbody>
<tr>
<td>Free residual chlorine</td>
<td>○</td>
<td>○</td>
<td>○</td>
<td>○</td>
<td></td>
</tr>
<tr>
<td>Turbidity</td>
<td>○</td>
<td>○</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Trihalomethanes</td>
<td>○</td>
<td>○</td>
<td>○</td>
<td>○</td>
<td></td>
</tr>
<tr>
<td>Soluble lead</td>
<td>○</td>
<td>○</td>
<td>○</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CAT 1)</td>
<td>○</td>
<td>○</td>
<td>○</td>
<td>○</td>
<td></td>
</tr>
<tr>
<td>2-MIB 2)</td>
<td>○</td>
<td>○</td>
<td>○</td>
<td>○</td>
<td></td>
</tr>
<tr>
<td>Tetrachloroethylene</td>
<td>○</td>
<td>○</td>
<td>○</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Trichloroethylene</td>
<td>○</td>
<td>○</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,1,1-Trichloroethane</td>
<td>○</td>
<td>○</td>
<td>○</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Iron (particle)</td>
<td>○</td>
<td>○</td>
<td>○</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aluminium (neutral)</td>
<td>○</td>
<td>○</td>
<td>○</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Recommended limit of use (l): 200 240 200 210

1) Simazine, 2) 2-methyl-isoborneol

**Removal efficiency of water purifier**

Four kinds of stock solutions (potassium iodide and cesium chloride / potassium iodate / strontium chloride and barium chloride / zirconium chloride) were prepared because iodide and cesium, and strontium and barium were similar in chemical forms (the former: alkali metal + halogen, the latter: alkaline earth metal + halogen), and added to the tap water to make test waters with sufficient concentration (40-50 μg/l) for evaluating the removal efficiency.

Each water purifier was washed with 500 ml of a test water, then another 500 ml of the same test water was applied to the water purifier and filtered without pressurization (Fig. 1). Water samples were collected before and after filtration to determine the concentrations of the target elements. This step was repeated for the 4 kinds of test waters. Thereafter, 36 l of tap water was applied to the water purifiers (total filtration volume was 40 l), then the test water filtrations and sample collections were conducted as described above. This step was repeated 5 times (40, 80, 120, 160 and/or 200 l).

Strontium, barium and zirconium were measured by inductively coupled plasma atomic emission spectrometry (ICP-AES, ICPE-9000, Shimadzu, Kyoto, Japan). Iodine and cesium were measured by inductively coupled plasma mass spectrometry (ICP-MS, SPQ9400, Seiko Instruments, Chiba, Japan) because ICP-AES has low sen-
sitivity to these 2 elements. As chemical characteristics of radionuclide are identical to its stable isotope, the removal efficiency was calculated as follows. \([A]\) and \([B]\) represent the concentration of each element after and before filtration, respectively.

\[
\text{Removal efficiency (\%)} = (1 - \frac{[A]}{[B]}) \times 100
\]

\textbf{Removal efficiency of adsorbent}

Zeolite A4, mordenite or activated carbon was stirred for 30 min in 200 or 600 ml of the test water with an additive rate from 0.001\% to 1.0\%, and measured for the pH. The treated test water of strontium, barium or zirconium was filtered with a glass filter (GS-25, Advantec Toyo, Tokyo, Japan). The test water of iodine or cesium was filtered with a cellulose acetate membrane filter (0.45 μm, Advantec Toyo), because the glass filter had an activity to adsorb cesium. There was no other adverse effect of the filters on the element concentrations. The filtrates were assayed by ICP-AES or ICP-MS, and the removal efficiency was calculated as above.

\textbf{Statistical analysis}

All experiments were conducted in duplicate or triplicate and statistical significance of the removal efficiency was confirmed by the t test. Difference in the removal efficiency between modes of water purifiers was examined by Mann-Whitney’s U test. Probability less than 0.05 was considered statistically significant.

\textbf{RESULTS}

\textbf{Removal efficiency of water purifier}

Iodide was removed by all of the water purifiers with the same efficiencies about 85\%, while iodate was removed with efficiencies about 40\% (Fig. 2). Cesium was removed by models B, C and D with efficiencies around 90\%, but the removal efficiency of model A was slightly less than the others (statistically significant). Barium was removed by all water purifiers with efficiencies higher than 85\%, and the efficiencies of models C and D were slightly but significantly higher than models A and B. The removal efficiencies for iodide, iodate, cesium and barium lasted at least 200 l, which is near the recommended limits for use of filter cartridges (Table 1), without decay.

As for strontium, models A and B showed the same removal efficiency of 70\% immediately after beginning of use, while models C and D showed higher efficiencies than former two (statistically significant). In particular, model D removed almost all strontium from drinking water. The removal efficiencies were decreased in accordance with use; however, model D kept the efficiency higher than 90\% even after 200 l filtration.

Zirconium was removed by models A and B with initial efficiencies of 30\% and 60\%, respectively. These efficiencies were increased with use, in particular, model B showed practically complete removal of zirconium after filtration of 40 l. On the other hand, models C and D hardly removed zirconium.

Filtration time of the 500 ml test water was 210, 270, 80 and 150 sec for model A, B, C and D, respectively, and it was prolonged to 260, 440, 120 and 160 sec after 200 l filtration.

\textbf{Removal efficiency of adsorbent}

Zeolite A4 efficiently removed cesium, strontium and barium from drinking water, and more than 90\% removal was achieved by addition of 0.01\% or higher. On the other hand, zeolite A4 had no removal effect on iodide, iodate and zirconium (Fig. 3).

Mordenite showed a removal efficiency for cesium as high as zeolite A4, while the removal efficiencies for strontium and barium were far less than those of zeolite A4. Iodide and iodate were hardly removed by mordenite.

Activated carbon showed removal effects on strontium and zirconium at high dose range. In particular, zirconium was almost completely removed by addition of activated carbon at 0.3\% or higher. Iodide, iodate and cesium were hardly removed by activated carbon.

Zeolite A4 elevated the pH of the test water, while mordenite and activated carbon slightly lowered the pH (Fig. 4). There was no difference in the pH among the kinds of test water.
DISCUSSION

The removal efficiency of radionuclide was evaluated by using its stable isotope, because chemical characteristics of radionuclide are identical to its stable isotope. In this approach, appropriate concentration of the element is required to estimate the removal efficiency accurately, although these elements other than zirconium were naturally included in the tap water at ppt - ppb levels. In the present study, 40-50 μg/l was adopted for the concentration of each element in the test water, and it had been confirmed in a preliminary experiment that there are no effects on the removal efficiency at least up to 100 μg/l. Therefore, the values evaluated by this method are sufficiently reliable.

Models A and B are equipped with activated carbon, ceramic and hollow fiber membrane as filter media; models C and D are equipped with activated carbon and ion exchanger. According to the manufacturer’s information, activated carbon is effective to remove residual chlorine and various organic compounds such as trihalomethanes and CAT, hollow fiber membrane can remove particulate larger than 0.1 μm, and ion exchanger and ceramic contribute to the removal of ionic lead.

Fig. 2. Removal efficiency of water purifier for iodine, cesium, strontium, barium and zirconium in drinking water. Mean and SD. Removal efficiencies were statistically significant (p < 0.05) except for those labeled with †.
Cesium, strontium and barium are alkali or alkaline-earth metals. They dissolve in neutral water in the form of monovalent or divalent cation when applied as chloride. Thus, the removal effects of water purifiers on these elements may be due to the ion exchanger or ceramic in the filter cartridge. The present results suggest ion exchanger is more effective than ceramic filter to remove these cations. On the other hand, involvement of activated carbon can not be excluded because it adsorbed strontium and barium in the results shown in Fig. 3. Hollow fiber membrane might not be involved in the removal effect on these elements, because their ionic radii are far smaller than the pore size of this membrane. This speculation is partially supported by our supplementary experiment where cellulose acetate membrane filter (0.45 μm) had no removal effect on these elements.

Zirconium chloride transforms into insoluble hydroxo complex (Mabuchi, 1994), when it is dissolved in neutral water. This is consistent with the present results where models A and B showed high removal efficiencies but models C and D were less effective, because models A
and B are equipped with hollow fiber membrane whereas models C and D have no function to remove particulate. The rising trend of the removal efficiencies of models A and B may result from clogging of the hollow fiber membrane, which was suggested by the prolongation of the filtration time.

It has been reported that activated carbon is effective to remove radioactive iodine (National Institute of Public Health, 2011), and the Japanese government has recommended the application of activated carbon at water purification plants in case of water contamination with radioactive iodine (Ministry of Health, Labour and Welfare, 2011-2). Therefore, the removal effect of water purifiers on iodine may result from the activity of activated carbon, which is equipped with all models.

On the other hand, the efficiencies for iodate were apparently less than those for iodide (Fig. 2). Chemical form of iodine is complicated in water; molecular iodine (I₂) hydrolyzes into iodide and hypoiodous acid (IO⁻), and they are partially oxidized into iodate (National Institute of Public Health, 2011). However, almost all of iodine is in the form of iodate in the tap water owing to the oxidation by chlorine (Kametani et al., 1992). This suggests that we can not expect such a high removal efficiency for iodine as observed for iodide.

Zeolite is a generic term of aluminosilicate whose chemical formula is expressed as Mₓ/(AlO₂)ₓ(SiO₂)ᵧ·zH₂O (M: cation, v: valency). It has cation exchange-ability in common. Zeolite A4 is a synthetic zeolite with high cation exchange capacity (CEC) of 5.5 meq/g (Breck, 1974). This indicates that only 0.01% zeolite (0.1 g/l) has an ability to capture cations up to 0.55 meq/l. Therefore, the removal efficiencies of zeolite A4 for cesium, strontium and barium are due to the high CEC.

Mordenite is a representative natural zeolite in Japan. Theoretical CEC of mordenite is 2.3 meq/g (Breck, 1974), however, CEC indicated on the product label of this mordenite is 1.5 meq/g presumably due to impurities. This value is 1/3.7 of zeolite A; however, its removal efficiency for cesium was almost the same as that of zeolite A4, while the efficiencies for strontium and barium were about 1/100 of those of zeolite A4. This suggests that mordenite has especially high affinity for cesium in comparison with strontium and barium.

The ineffectiveness of zeolite A4 on zirconium is consistent with that zirconium is expected to be insoluble hydroxo complex in neutral water. If so, it is not explainable that mordenite has a removal effect on zirconium. It remained unclear why the reaction with zirconium is different between synthetic zeolite and natural zeolite. On the other hand, it is reasonable that zeolite A4 and mordenite have little effect on iodine, which is in anionic forms in water.

In general, pH of water may affect the adsorbability of adsorbents. However, pH of the test water remained within the range of legal regulation of tap water (5.8-8.6) up to the concentration of 0.03% for zeolite A4 or 0.3% for mordenite and activated carbon. Furthermore, zeolite A4 and mordenite showed the same characteristics in cesium adsorption in spite of their contrary effects on pH. Therefore, the change of pH is suggested to have little effect on the removal efficiencies of adsorbents at least in this experiment.

In case of radioactive contamination of tap water, water purifiers may be available for convenient decontamination of drinking water in the home. Application of synthetic or natural zeolite at water purification plants may be also effective to remove radioactive cesium, strontium and/or barium.

REFERENCES


