Status of Contaminated Water Treatment and Tritium at Fukushima Daiichi Nuclear Power Station

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Content

1. Reactor Cooling Status
2. Contaminated Water Status
3. Tritium Status
1. Reactor Cooling Status: Cooling by Recirculating Cooling Water

Reactors are maintained in a low temperature stable state through continuous cooling which recirculates cooling water and injects it into the reactors.

- Reactor cooling water injection: ~400 m³/day
- Cooling by recirculating cooling water: ~800 m³/day
- Desalination: Reverse osmosis, Evaporative concentration
- Treated water (contaminated water)
- Storage tanks
- Multi-nuclide removal system (ALPS)
- Interim Storage Facility waste sludge, waste adsorbent, etc.
1. Reactor Cooling Status: Individual Unit Status

- Cold shutdown state continues to be maintained at each unit

<table>
<thead>
<tr>
<th></th>
<th></th>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>~16°C</td>
<td>~16°C</td>
<td>~20°C</td>
<td>Feed water system: 2.3m³/h</td>
</tr>
<tr>
<td>2</td>
<td>~25°C</td>
<td>~25°C</td>
<td>~15°C</td>
<td>Core spray system: 2.0m³/h</td>
</tr>
<tr>
<td>3</td>
<td>~22°C</td>
<td>~20°C</td>
<td>~15°C</td>
<td>Core spray system: 2.5m³/h</td>
</tr>
<tr>
<td>4</td>
<td>—</td>
<td>—</td>
<td>~19°C</td>
<td>—</td>
</tr>
</tbody>
</table>

2. Contaminated Water Status: Overview of Contaminated Water Treatment

- Cesium, which is a major radiation source (gamma ray), is reduced by cesium removal systems.
- Saline matter is removed by the desalination system as the water will be used for cooling the reactors.
- The concentration of radioactive materials (excluding tritium) in water, which is retained in tanks, is reduced by the multi-nuclide removal system (ALPS).

Radioactivity Concentrations of Key Nuclides

- Cesium, which is a major radiation source (gamma ray), is reduced by cesium removal systems.
- Saline matter is removed by the desalination system as the water will be used for cooling the reactors.
- The concentration of radioactive materials (excluding tritium) in water, which is retained in tanks, is reduced by the multi-nuclide removal system (ALPS).

- Sampling date: Nov. 5, 2013 (Apr. 9-12, 2013 for ALPS outlet water)
- Data for cesium removal systems outlet water is used for concentration of gross beta and H-3 in retained water in buildings.
- The detectable limit value is used for cases where concentration is below the detectable limit.
2. Contaminated Water Status: Cesium Removal Systems

- Usage commenced: June 17, 2011 (Kurion) & Aug. 19, 2011 (SARRY)
- Treatment capacity: 1,200m3/day <respective rated treatment capacity (when one pump is operating)>

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2. Contaminated Water Status: Desalination System (Reverse Osmosis (RO))

- Salt is removed to make fresh water by using the properties of reverse osmosis membranes, which do not allow ions, saline or other non-water impurities to pass through.
- The system is comprised of a receiving tank, filtration system, RO membranes, treated water tank and other components.
2. Contaminated Water Status: Multi-Nuclide Removal System (ALPS)

- Removes radioactive materials in contaminated water (excluding tritium)
- Testing underway using water containing radioactive materials

ALPS hot tests were conducted using contaminated water (RO concentrated brine). Removal performance was assessed for the 62 nuclides targeted for removal. Analysis results of treated water during hot tests of subsystems A, B and C have confirmed the following.

- Radiation concentration of Sr-90, a major nuclide, was reduced to 1/100millionth~1/billionth
- Co-60, Ru-106(Rh-106), Sb-125(Te-125m) and I-129 were detected at comparatively high levels

Nuclides in parentheses indicate radioactive equilibrium

※Selection of Nuclides for Removal (Excerpt of items indicated in Implementation Plan)

【Nuclides Reviewed】
- Radioactive materials having their origin in fuel inside the reactors of Units 1~3 (FP nuclides).
- Radioactive materials having their origin in corrosion products contained in water retained during plant operation (CP nuclides).

【Estimating concentration】
- FP nuclides: Nuclides, which are assumed to be present at significant concentrations based on the results of core inventory assessments, are selected and their concentrations estimated based on the results of accumulated water measurements (2011/3) and core inventory assessments.
- CP nuclides: Selection is made of nuclides, which are contained in water retained in reactors during plant operation, and nuclides, which are present in water retained in concentrated liquid waste tanks and mixed with accumulated water when it was transferred to the high temperature incinerator building, and the results of measurements of such retained waters are used to estimate the concentrations in accumulated water.

【Selecting nuclides for removal】
- Decay during the period from accident occurrence to ALPS operation (approx. 1 year) is assessed to estimate the concentrations.
- Nuclides whose estimated concentration exceeds 1/100 of the notification concentration limit are selected as nuclides for removal which are present at significant concentrations.
- However, as tritium is difficult to remove, it is excluded from the nuclides subject to removal.
2. Contaminated Water Status: Evaluation of Removal Performance in Hot Tests

Ratio to Notification Concentration of ALPS Treated Water

- Cs-137
- Sr-90
- I-129
- Ru-106
- Co-60
- Sr-125
- Other radionuclides
- Total of 6 nuclides
- Ref/H-3
- Ref/C-14

Ratio to enforcement concentration

Before ALPS treatment
After ALPS treatment

Sampling dates:
- Sept. 30~Oct. 4, 2013 (time of subsystem C hot test)
- Nov. 15, 2013
- Jan. 15, 2014
- Feb. 14, 2013

The detectable limit is used for cases where concentration is below the detectable limit

2. Contaminated Water Status: Review of Removal Performance Improvement Measures (Overview of In-plant Flow Passing Testing)

- **Review of Performance Improvement Measures**
  - There are prospects for improving removal performance by passing nuclides having relatively high radiation concentrations through activated carbon-type adsorbent
  - In laboratory tests, the maintenance of removal performance over a long period of time when being passed by large amounts of water could not be verified
  - Accordingly, test devices, which are filled with an activated carbon-type adsorbent and other materials, are connected to the actual system to conduct flow passing tests (in-plant flow passing tests) to verify the maintenance of removal performance
  - In the in-plant flow passing tests, verification will also be conducted of alternative adsorbents, which are expected to improve removal performance, in addition to activated carbon-type adsorbent

Test system

- Test device installed on subsystem A. Flow passing test conducted 1/24~3/18.
Based on test results, improved removal performance (sum of notification concentration limits from the current approximately 6 to 0.5~0.6 after improvements) can be expected to be obtained by adding an additional two adsorption towers and modifying the tower configuration as in the diagram below.

**Co-60**
There are prospects for removal using activated carbon (confirmation of presence of colloidal-form radioactive materials).
If there is an increase of two columns of activated carbon, higher removal performance can be expected to be obtained.

**Sb-125**
It is estimated that there is insufficient adsorption capacity with the current two towers of activated carbon and two towers of adsorbent for Sb, etc.
If there is an increase to four towers of activated carbon and four towers of adsorbent for Sb, etc., then higher removal performance can be expected to be obtained.

**I-129**
In addition to the formation of iodine ions and colloids, it is estimated that there are iodate ions present.
The results of test simulating "iodate ion adsorbent" + "silver-loaded adsorbent" + "activated carbon" confirmed a higher removal performance when water was passed through for approximately 10 days.
In-plant tests are scheduled to be continued to verify lifespan.

**Ru-106**
Based on cold tests, media capable of removing Ru was selected (verification scheduled to be conducted using in-plant tests).

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**2. Contaminated Water Status:**

- **Total storage capacity**: approx. 490,000m³
- **Total storage volume**: approx. 460,000m³
- **Plan to increase capacity to 800,000m³** (completion target: end of FY2014)

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**Storage of Contaminated Water**

- **Steel square tanks**
- **Steel cylindrical tanks (flange joint)**
- **Steel cylindrical tanks (welded)**
- **Steel horizontal tanks**

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**Storage capacity by tank type**

- Steel square tanks: approx. 3,000m³
- Steel cylindrical tanks (flange): approx. 300,000m³
- Steel cylindrical tanks (welded): approx. 140,000m³
- Steel horizontal tanks: approx. 40,000m³

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*As of April 22, 2013*
2. Contaminated Water Status: Volume of Treated Water (Water Stored in Tanks)

- Total volume of treated water (concentrated brine, concentrated liquid waste, ALPS treated water, and fresh water): approx. 460,000m³.
- Of this, total volume of ALPS treated water: approx. 73,000m³. ※As of April 22, 2014
  (By end of FY2014, ALPS treatment of all tank water is scheduled to be completed)

![Map of Contaminated Water]

Volume of Treated Water Stored ※1

- **Treated water**: 458,678m³
- **ALPS treated water**: 73,662m³

![Graph showing the volume of treated water]

Source: Decommissioning Promotion Council data (status of accumulated water treatment)

※1: ① is volume of building accumulated water stored: approx. 94,640m³
※2: ② is total for concentrated brine and concentrated liquid waste

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3. Tritium Status: Concentration of Tritium in Newly RO Treated Water

Concentration of Tritium in Newly RO Treated Water

$$y = 4 \times 10^6 e^{0.0764x}$$

March 2016: $6.71 \times 10^4$ Bq/liter

3. Tritium Status: Cumulative Amount of Tritium Stored in Tanks at Fukushima Daiichi NPS

Cumulative Amount of Tritium

- Case A: groundwater bypass implemented, sub-drains pumped out, rainwater drained, and groundwater drains drained
- Case B: groundwater bypass not implemented, sub-drains not pumped out, rainwater drained, and storage of groundwater in drains

In addition, it is estimated that there will be $6.08 \times 10^{14}$ Bq in the R/B, T/B, Central RW and HIT buildings by March 2016.
3. Tritium Status: Salinity of ALPS Treated Water

Source: Decommissioning Promotion Council data (status of accumulated water treatment); concentrated brine after RO treatment has twice the saline matter as that prior to treatment, therefore the values noted in the data were doubled and then plotted.

3. Tritium Status: Total Tritium Amount

Amount of tritium at Fukushima Daiichi Nuclear Power Station (Units 1~4) is estimated to be as follows. As of March 25, 2014

<table>
<thead>
<tr>
<th>Points estimated</th>
<th>Tritium amount</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[Bq]</td>
<td>[g]×1</td>
</tr>
<tr>
<td>Total amount</td>
<td>~3.4 × 10^{15}</td>
<td>T: ~9.5</td>
</tr>
<tr>
<td>[Break down]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>• Water accumulated in tanks</td>
<td>~8.3 × 10^{14}</td>
<td>T: ~2.3</td>
</tr>
<tr>
<td>• Water accumulated in buildings</td>
<td>~5.0 × 10^{13}</td>
<td>T: ~0.14</td>
</tr>
<tr>
<td>• Water in seawater pipe trenches</td>
<td>~4.6 × 10^{13}</td>
<td>T: ~0.14</td>
</tr>
<tr>
<td>• Other</td>
<td>~2.5 × 10^{15}</td>
<td>T: ~6.9</td>
</tr>
</tbody>
</table>

※1: Weight of tritium atoms (figure in parentheses shows the weight corresponding to the THO form)
※2: ORIGEN 2 is used to assess the in-core tritium inventory at the time of the accident (see pp. 10~12)
※3: Estimated based on desalination system outlet concentration data and volume of water stored in tanks (see pp. 13~14)
※4: Estimated based on desalination system outlet concentration data (March 2014) and volume of water accumulated in buildings (approx. 92,000m³)
※5: Estimated based on desalination system outlet concentration data (September 2011) and volume of water accumulated in trenches (approx. 11,000m³)
※6: Calculated by subtracting amount of tritium in water stored in tanks, water accumulated in buildings and trenches from total amount (it is estimated that tritium other than that in tanks, buildings and trenches is mainly present in fuel debris and other such matter)
### 3. Tritium Status: Chemical Properties of ALPS Treated Water

<table>
<thead>
<tr>
<th>General properties</th>
<th>ALPS Treated Water</th>
<th>[Ref]* Guidelines for General Drainage Channels and Discharged Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample date/time</td>
<td>April 16, 2013 10:30</td>
<td>April 18, 2013 11:30</td>
</tr>
<tr>
<td>Conductivity (μ S/cm)</td>
<td>6220</td>
<td>6200</td>
</tr>
<tr>
<td>Chlorine (ppm)</td>
<td>2100</td>
<td>1900</td>
</tr>
<tr>
<td>pH</td>
<td>7.6</td>
<td>7.4</td>
</tr>
<tr>
<td>Suspended solids (mg/L)</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Chemical oxygen demand (COD) (mg/L)</td>
<td>&lt;1</td>
<td>1</td>
</tr>
</tbody>
</table>

**Items with possible impact on environment**

<table>
<thead>
<tr>
<th>Items with possible impact on tritium separation, etc.</th>
<th>Concentration of ionic species (ppm)</th>
<th>Na⁺</th>
<th>NH₄⁺</th>
<th>NO₂⁻</th>
<th>NO₃⁻</th>
<th>SO₄²⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>1480</td>
<td>30</td>
<td>0</td>
<td>0</td>
<td>760</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1590</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>610</td>
</tr>
</tbody>
</table>

※According to Guidelines for General Drainage Channels and Discharged Water prescribed by in Appendix 5 of Article 25 of the Ordinance for Enforcement Concerning Conservation, etc. of Living Environment in Fukushima Prefecture

### 3. Tritium Status: Research of Remove Technology

Research and development of handling are performed by the atomic power (Heavy Water reactor etc.) which needs to separate tritium as impurities, and the nuclear fusion which treats tritium as a fuel substance.

- **Heavy Water Reactor (CANDU type, Advanced Thermal Reactor “Fugen”, etc.)**
  - Deuterium will generate tritium, if a neutron is absorbed. In order to separate tritium from heavy water, the isotope separation of DTO-D₂O is required.
- **Nuclear Fusion Reactor**
  - Technology of fuel treatment
  - Unreacted fuel is processed and it uses efficiently.
  - Recovery of waste water and waste gaseous
  - Recovery from tritium contamination in Groundwater
  - Hanford site (DOE)
  - Study in EPRI

Such technology is investigated focusing on literature documentation and an interview.

- **Literature documentation**
  - The technology adopted the past research and in and outside is investigated for a paper etc.
- **Interview**
  - Directly, the talk is heard from a domestic researcher and an engineer.
  - Example: Researcher, Expert, Institution of research (JAEA, NIRS, etc.)

The thing applicable by the present is not found.
3. Tritium Status: Example of remove technology

As main remove technology, some were following as a result of investigation so far.

1. Water Distillation
   - Example: · · · ··Tokai Reprocess (JAEA), Manhattan project (USA), etc.

2. Cryogenic Distillation
   - Example: · · · ··JRR-3M (JAEA), Institute Laue-Langevin (France), etc.

3. Vapor Phase Catalytic Exchange (VPCE)
   - Example: · · · ··Darlington NPS (Canada), Institute Laue-Langevin (France), etc.

4. Liquid Phase Catalytic Exchange (LPCE)
   - Example: · · · ··Chalk River Laboratories (Canada), Wolsong NPS (Korea), etc.

5. Electrolysis
   - Example: · · · ·Can’t find

6. Combined Electrolysis Catalytic Exchange (CECE)
   - Example: · · · ·“Fugen” Upglader II (JAEA), etc.

7. Bithermal Hydrogen-Water Process
   - Example: · · · ·Can’t find

Besides method: Isotope Effect (Girdler Sulfide Process, Ammonia Process, Amine Process, etc), Adsorption remove under deep low temperature, etc. Anything method is troublesome and small throughput.
3. Tritium Status: **Tritium Remove Technology**

5. Electrolysis
   - It uses that a heavy constituent decreases compared with the corresponding contrast in an electrolysis solution for the hydrogen gas emitted with cathode.
   - Energy consumed is large, and if a multi-stage cascade is built, the amount of consumption will become serious. Furthermore, it is easy to be subject to the influence of impurities, and independent use is disadvantageous.

6. Combined Electrolysis Catalytic Exchange (CECE)
   - What combined two kinds of technology.
   - With the technology for high concentration tritium, a throughput has a maximum.
   - The process of removing alkali is required for the alkali electrolysis vessel adopted by “Fugen.”

7. Bithermal Hydrogen-Water Process
   - The method using the isotopic chemistry balance shift of a high temperature state and a cold condition.
   - It is a thing aiming at heavy water manufacture, and when applying to tritium, it has a difficulty in control and the operativity of concentration.

3. Tritium Status: **Parallel of remover concentration**

Although some are remove to an environmental level (several Bq/Liter) theoretically, when performing processing on an industrial scale, equipment and consumption energy become huge. Only a thing deeper than concentration of Fukushima Daiichi can remove by the remove equipment put in practical use on a scale of industry. Remove can’t at comparatively low concentration of Fukushima Daiichi.

reference: JAERI-M 88-168, WM’06 Conference, T.Sugiyama (Nagoya university), Development of Water Distillation Column analysis, Committee of provision for contaminated water treatment (Ministry of Economy, Trade and Industry)
Dissipation

- Evaluation of the dissipation behavior after release
- Evaluation of impacts on human body, etc. after dissipation
- Development of a system to trace the behavior after dissipation

Gas after solidification

- Release to the Atmosphere
- Tritiated Water
  - Volume Reduction
  - Dilution

- Dilution of highly concentrated tritiated water
- Concentrated Tritiated Water

- Dilution of highly concentrated tritiated water
- Tritiated Water after
  - Dilution
  - Volume Reduction

Storage of small amount of highly concentrated tritiated water

- Storage of small amount of highly concentrated tritiated water
- Concentrated Tritiated Water

Storage of significant amount of tritiated water

- Storage of significant amount of tritiated water
- Concentrated Tritiated Water

Volume Reduction

- Dilution of highly concentrated tritiated water
- Tritiated Water after
  - Dilution
  - Volume Reduction

Isotopic Reduction

- Isotopic Reduction
- Tritiated Water

Removal of radioactive nuclides except tritium

- Tritiated Water
- Isotopic separation

Further Volume Reduction is possible by repeating Isotopic Separation

Separation performance of tritium: Separation factor higher than 100

Adoption entrepreneur (August 26, 2014)

Kurion, Inc. 【USA】

GE Hitachi Nuclear Energy Canada Inc. 【Canada】

Federal State Unitary Enterprise “Radioactive Waste Management Enterprise “RosRAD”” 【Russia】

Separation method

Combined Electrolysis Catalytic Exchange (CECE)

Water Distillation

Combination of CECE and Water Distillation

The Mitsubishi Research Institute, Inc., having been selected by the Agency for Natural Resources and Energy (ANRE, METI, Japan), is now executing the tasks of the Project Management Office for the "Project of Decommissioning and Contaminated Water Management". In this project, based on the "Grant Policy for Subsidy for the Project of Decommissioning and Contaminated Water Management", we are assisting activities in support of the development of technologies that will be useful in decommissioning and contaminated water management. Through this, we aim to improve the level of science and technology and to advance decommissioning and contaminated water management smoothly in Japan.

At this time we are proceeding with the RFP (Request for Proposal) for entities to receive subsidies and implement the "Verification of technologies for contaminated water management (Demonstration Project for Verification Tests of Tritium Separation Technologies)" as the fifth RFP. If you are interested in responding to this RFP, please take into consideration the information provided in this document as well as the detailed information provided in the separate document "Guidelines for applying to the "Verification of technologies for contaminated water management project" in the FY2013 Supplementary Budget".

Duration of the project: From the date of the grant decision to March 31st, 2016

Separation factor higher than 100
Sources of Tritium Production at Nuclear Power Stations

1. Production by ternary fission of fuel
   - Tritium is produced as a fission product of $^{235}U$ and $^{239}Pu$ during "burning (fission)". The amount is 0.013% of $^{235}U$ and 0.023% of $^{239}Pu$, and $^{239}Pu$ in fuel becomes predominant as the fuel burns further. The amount of tritium generated per 1MW with assuming 0.018% as the average is as follows.

   $$N_F \times 1.8 \times 10^{-3} \times \lambda = 1.01 \times 10^5 \text{Bq/s} \cdot \text{MWt}$$

   NF: No. of fissions per 1MWt in 1 second = $3.15 \times 10^{16} / \text{s} \cdot \text{MWt}$

2. Production by neutron irradiation of boron-10 contained in boron carbide control rods
   - Tritium is produced by the following reaction inside the poison rods of control rods using $B_4C$ (boron carbide) for neutron absorption
     
     $$^{10}B + n \rightarrow ^3H + ^2He$$
     $$^{10}B + n \rightarrow ^7Li + ^4He$$
     $$^7Li + n \rightarrow ^3H + ^2He + n$$
   - In 1 g of $B_4C$ irradiated until $^{10}B$ decreases approximately 50%, a conservative assessment puts the amount of tritium produced at $1.48 \times 10^9 \text{Bq/g B}_4\text{C}$, but, even if the control rod is damaged, the tritium will not be released all at once.

3. Activation of reactor water (production by neutron irradiation into heavy water, etc.)
   - Tritium is produced by neutron irradiation into heavy water in the reactor water. The amount of tritium generated into heavy water is calculated using the following equation.

   $$^2H + n \rightarrow ^3H + \gamma$$

   $$N^3H = \Sigma(D_{2}O) \times \varphi \times V \times \rho \times (D/H) \times t$$

   - The amount of tritium produced inside a reactor is approximately as given below.

<table>
<thead>
<tr>
<th>Amount of tritium produced</th>
<th>500,000kWe</th>
<th>800,000kWe</th>
<th>1,100,000kWe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bq/month</td>
<td>4.07E+13</td>
<td>6.29E+13</td>
<td>8.51E+13</td>
</tr>
</tbody>
</table>

**Reference** 1. Tritium Produced at Nuclear Power Stations (1)

[Image 37x61 to 558x63]
[Image 505x378 to 556x395]
[Image 37x470 to 558x472]
[Image 505x786 to 556x804]
The in-core tritium inventory is mainly that which is produced by ternary fission. Thus, ORIGEN 2 (nuclear fuel burn-up calculation code) was used to perform a detailed assessment of the time of the accident, which resulted in the following.

Of the tritium found as the result of assessment prior to the accident, approximately 60% is believed to be occluded in fuel rod cladding.

Currently (end of March 2014), the total amount of tritium contained in water stored in tanks is estimated to be \(8.34 \times 10^{14}\) Bq. By the end of February 2016, this amount is estimated to be approximately \(9 \times 10^{14}\) Bq.

The concentration of tritium contained in water which will be newly treated at that time (end of February 2016) is estimated to be \(6.7 \times 10^4\) Bq/liter.

\[3.4 \times 10^{15}\text{Bq}, \text{which is the total amount of tritium in Units 1~3 in the above table, is an amount equivalent to a tritium atoms' weight of 9.5g. (If tritium is present in “THO” form, then the atoms’s weight is equivalent to 63.3g.)}\]

<table>
<thead>
<tr>
<th></th>
<th>Unit 1</th>
<th>Unit 2</th>
<th>Unit 3</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>TEPCO</td>
<td>1.0E+15</td>
<td>1.2E+15</td>
<td>1.2E+15</td>
<td>3.4E+15</td>
</tr>
<tr>
<td>&lt;Ref&gt;</td>
<td>JAEA'</td>
<td>9.4E+14</td>
<td>1.2E+15</td>
<td>3.3E+15</td>
</tr>
</tbody>
</table>


\* Toshiba Corporation “Compaction Tests of Irradiated Hulls” (report for work performed under contract with JAEA (formerly, the Power Reactor and Nuclear Fuel Development Corporation) September 1996.