Analysis of a Uranium Solution for Evaluating the Total Number of Fissions in the JCO Criticality Accident in Tokai-mura

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JCO criticality accident/Analysis/Total number of fissions/Uranium/Fission products

The uranium solution in the precipitation tank in the JCO’s uranium conversion facility was analyzed in order to evaluate the total number of fissions in the criticality accident. Two analytical groups at JAERI performed chemical analyses independently in order to check the validity of the results: the concentration of the fission products (95Zr, 99Mo, 103Ru, 131I, 140Ba, etc), uranium, boron and impurity elements in the solution. The analytical results obtained by the two groups were almost in agreement within the analytical error. The number of fissions per one gram of uranium in the accident was determined to be (1.5 ± 0.1) × 1014. Also, the total number of events was evaluated to be (2.5 ± 0.1) × 1018 fissions using the total amount of uranium (16.6 kg) fed into the precipitation tank at the accident.

INTRODUCTION

On September 30, 1999, at 10:35 local time, a criticality accident occurred at a uranium fuel fabrication plant operated by JCO Co., Ltd. Tokai-mura, Japan. Pouring a large amount (18.8 weight %) of a 235U-enriched uranyl nitrate solution into the precipitation tank led to the nuclear criticality. It continued for about 20 hours, until the chain reaction was terminated at about 6:15, on October 1. After termination, re-criticality of the uranium solution caused by its temperature decrease was of great concern. To prevent re-criticality, an aqueous solution mixture of boric acid and sodium tetraborate was added to the accident solution. Detailed information on the
accident can be obtained elsewhere\textsuperscript{1,2}).

It is very important to know the total number of fission events in the accident for evaluating its environmental impact. Sampling of the uranium solution in the precipitation tank was performed on 20 October, about 20 days after the accident. Analytical work on the uranium solution was carried out in order to evaluate the total number of fission events, the possibility of re-criticality of the solution in the precipitation tank and the source term on the released fraction of volatile fission products in the criticality accident.

This paper presents the analytical methods used for the uranium solution, the analytical results, and an evaluation of the total number of fissions in the accident. In addition, the source term on released fission products during the accident is also described.

**EXPERIMENTAL**

**Sampling**

About 50 ml portions of the uranium solution was taken from the precipitation tank in the conversion test building of JCO Co. Ltd. on October 20, 1999. The sample solution was taken from the middle part of the uranium solution in the tank\textsuperscript{2)}\textsuperscript{2). The sample solution was transported to the Nuclear Fuel Cycle Safety Engineering Research Facility (NUCEF) in the Tokai establishment of Japan Atomic Energy Research Institute (JAERI). There were minute amounts of precipitates at the bottom of the sample solution. Thus, the solution was filtered through a membrane filter with a pore size of 0.2 µm to remove any precipitate before the analysis. Two analytical groups (A and B) in JAERI independently carried out analyses on the sample solution to check the validity of the analytical results. The following measurements were carried out: the concentration of the fission products by gamma-ray spectrometry, uranium by isotope dilution mass spectrometry (IDMS) and redox potentiometric titration, boron and other elements by inductively coupled plasma emission spectrometry (ICP-AES) and isotope ratio of uranium by thermal ionization mass spectrometry (TIMS).

**Measurements of fission products**

Both of the analytical groups measured the fission products by gamma-ray spectrometry with a high-purity germanium detector (Group A, GMX-20190-P-Plus; Group B, GMX-20195-P) coupled to a spectroscopy amplifier (Group A, ORTEC-672; Group B, ORTEC-673) which was connected to an ORTEC-7800 multi-channel analyzer.

The sample preparation and calibration method in gamma-ray spectrometry by each analytical group is briefly written below.

Group A: 1ml of the sample solution was taken into a 20 ml vial and diluted to 5 ml with 1 M nitric acid. Also, a 1 ml aliquot of the diluted uranium solution was taken into another 20 ml vial and diluted to 5 ml with 5 M nitric acid for subsequent gamma-ray spectrometry. The counting time was 3,600 seconds, which was repeated five times. The detection efficiency was calibrated using a standard mixture of radionuclides\textsuperscript{3)}\textsuperscript{3} (\textsuperscript{241}Am, \textsuperscript{235}U, \textsuperscript{238}U(\textsuperscript{234}Th), \textsuperscript{137}Cs and \textsuperscript{60}Co) which were purchased from LMRI, France. The resulting gamma-ray spectrum was analyzed by using
Group B: 1ml of the uranium solution was taken into a polyethylene tube (14 mm inner diameter) for gamma-ray spectrometry. The counting time was for 70,000 seconds. The gamma-ray spectrum obtained was then analyzed by using a spectrum analysis code, BOB, developed by JAERI. The detection efficiency was calibrated using a working standard solution prepared by adding radionuclides ($^{106}$Ru, $^{134}$Cs, $^{137}$Cs, $^{154}$Eu) separated from spent fuel to 1 ml of the uranium solution (240mgU/ml) in a polyethylene tube having the same size as that of the sample. In parallel, the same amount of radionuclides was placed onto a tantalum disk. Its accurate radioactivity was also determined using a standard source made from a known amount of radionuclide reference standards: $^{152}$Eu, $^{137}$Cs (LMRI, France).

**Determination of the concentration and isotopic composition of uranium**

For determining the uranium concentration of the sample solution, group A used a modified ferrous sulfate reduction in phosphoric acid and a dichromate titration method, group B applied the IDMS analysis using a high-purity natural uranium certified reference material (JAERI U4) as a spike. Both groups used TIMS (Finnigan-MAT 262 multiple collector mass spectrometer) for isotope ratio measurements of uranium. Group A applied the total-evaporation technique to obtain an accurate isotope ratio without any fractionation correction of the mass spectrometer. On the other hand, group B used a conventional technique with the use of an isotopic standard reference material (NBL CRM U 500) for calibrating the mass bias.

**Determination of boron and metal impurities.**

For determining these elements, both groups used ICP-atomic emission spectrometry. The sample solution was diluted by 100 to 200 fold prior to the measurements. Standard solutions for the calibration were prepared by adding known amounts of elements to a uranium solution with a similar concentration to the accident solution.

**RESULTS AND DISCUSSION**

Table 1 shows the concentrations of fission products obtained by the two analytical groups. The errors are in relative standard deviation ($\sigma$). Although it would seem that a small bias is present between the data obtained by two groups, the agreement between the data is almost within the analytical errors. The analytical results of the concentration and isotopic composition of uranium in the sample solutions obtained by the two groups were in complete agreement with each other: the concentration of uranium was 279 ± 0.5 g/L, and $^{235}$U enrichment was 18.83 ± 0.02 weight%. The results of boron and other impurity elements for the two groups were also in good agreement. The result of the boron concentration, 5.6 g/L, confirmed that the accident solution could be kept in a subcritical state.

The number of fissions per one gram of uranium in the accident solution was evaluated based on the analytical results of non-volatile fission products. Four nuclides were selected for a calculation: $^{95}$Zr, $^{99}$Mo, $^{103}$Ru and $^{147}$Nd. Although the fission products were continually produced
Table 1. Concentration of fission products in the JCO uranium solution.

<table>
<thead>
<tr>
<th>Nuclide</th>
<th>Group A Concentration [Bq/ml]</th>
<th>Error [%], RSD</th>
<th>Group A Concentration [Bq/ml]</th>
<th>Error [%], RSD</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{95}\text{Zr}$</td>
<td>$2.15 \times 10^5$</td>
<td>5</td>
<td>$2.63 \times 10^5$</td>
<td>5</td>
</tr>
<tr>
<td>$^{99}\text{Mo}$</td>
<td>$4.34 \times 10^4$</td>
<td>6</td>
<td>$4.64 \times 10^4$</td>
<td>7</td>
</tr>
<tr>
<td>$^{103}\text{Ru}$</td>
<td>$1.77 \times 10^5$</td>
<td>5</td>
<td>$1.96 \times 10^5$</td>
<td>5</td>
</tr>
<tr>
<td>$^{131}\text{I}$</td>
<td>$1.89 \times 10^5$</td>
<td>5</td>
<td>$2.18 \times 10^5$</td>
<td>6</td>
</tr>
<tr>
<td>$^{132}\text{Te}$</td>
<td>N.I.</td>
<td>–</td>
<td>$6.77 \times 10^4$</td>
<td>5</td>
</tr>
<tr>
<td>$^{137}\text{Cs}$</td>
<td>$1.48 \times 10^3$</td>
<td>11</td>
<td>N.I.</td>
<td>–</td>
</tr>
<tr>
<td>$^{141}\text{Ce}$</td>
<td>N.I.</td>
<td>–</td>
<td>$4.38 \times 10^4$</td>
<td>6</td>
</tr>
<tr>
<td>$^{144}\text{Ce}$</td>
<td>$6.91 \times 10^4$</td>
<td>10</td>
<td>N.I.</td>
<td>–</td>
</tr>
<tr>
<td>$^{147}\text{Nd}$</td>
<td>$5.31 \times 10^5$</td>
<td>5</td>
<td>$5.97 \times 10^5$</td>
<td>6</td>
</tr>
<tr>
<td>$^{140}\text{Ba}$</td>
<td>$1.86 \times 10^5$</td>
<td>5</td>
<td>$2.04 \times 10^5$</td>
<td>4</td>
</tr>
</tbody>
</table>

RSD: relative standard deviation; N.I.: not identified

Group A: corrected values for decay at 16:00 on 20 October (measured at 10:36 on 21 October). Group B: measured value at 17:44 on 20 October.

during the about 20 hours of criticality, they were calculated to be produced at once at the beginning of the accident: at 10:35 on 30 September. The calculated results of the number of fissions, together with the concentration of fission products, are given in Table 2. The value of the concentration for each nuclide is an average between two groups. Its error was calculated by using

$$\text{Error}(\%) = \sqrt{\frac{\sum \sigma_i^2}{n}},$$

where $\sigma_i$ and $n$ denote the relative standard deviation(%) of each group and the number of groups, respectively. There is a good agreement among the number of fission events calculated from the concentration of each fission product using its half-life$^9)$ and the fission yield$^{10})$. This clearly reveals that each nuclide produced was homogeneously distributed and retained in the uranium solution in the precipitation tank. The average of the number of fission reactions per one gram of uranium was calculated to be $(1.5 \pm 0.1) \times 10^{14}$, in which the error in the relative standard deviation was calculated from the error for each nuclide using equation (1) in a similar manner.

Table 2. Number of fission events estimated by the fission products.

<table>
<thead>
<tr>
<th>Fission products</th>
<th>Half life$^9)$ [hours]</th>
<th>Fission Yield$^{10)}$ [%]</th>
<th>Concentration*1 [Bq/ml]</th>
<th>Error [%]</th>
<th>Number of fissions per g uranium [fission/g-U]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{95}\text{Zr}$</td>
<td>1536.5</td>
<td>6.520</td>
<td>$3.28 \times 10^5$</td>
<td>5.0</td>
<td>$(1.44 \pm 0.07) \times 10^{14}$</td>
</tr>
<tr>
<td>$^{141}\text{Nd}$</td>
<td>263.5</td>
<td>2.270</td>
<td>$7.01 \times 10^5$</td>
<td>5.1</td>
<td>$(1.51 \pm 0.08) \times 10^{14}$</td>
</tr>
</tbody>
</table>

* 1: Normalized at 10:35 on 30 September.
average of the number of fission reactions per one gram of uranium is considered to be the maximum, because it is presumed that all of the fission products were produced instantaneously at the beginning of the criticality accident. The total reaction was estimated to be \((2.5 \pm 0.1) \times 10^{18}\) fissions using the amount of uranium (16.6 kg) in the precipitation tank at the accident. This uranium amount was obtained by subtracting the amount of the uranium (182.7 g) in a stainless-steel beaker left outside the tank from the total amount of uranium (16.77 kg) that had planned to be fed into the tank on the day of the accident. The total number of fission events given in the present paper is in very good agreement with that obtained from analyses of the activation products in the stainless-steel net near the precipitation tank, which is \(2.4 \times 10^{18}\) fissions\(^2,11\). At least 21 criticality accidents at nuclear fuel processing facilities have been reported around the world. The JCO Criticality Accident is the third largest one. In most cases, the total number of fission events was less than \(10^{18}\) fissions\(^12\).

The concentrations of \(^{131}\text{I}\), \(^{137}\text{Cs}\) and \(^{140}\text{Ba}\) in the accident solution were obtained. Latter two nuclides were produced by \(\beta^-\) decays via \(\text{Xe}\), i.e., \(^{137}\text{Xe}\) (half life: 3.81 m) \(^{137}\text{Cs}\) and \(^{140}\text{Xe}\) (half life: 13.6 s) \(^{140}\text{Cs}\) (63.7 s) \(^{140}\text{Ba}\) (12.75 d), respectively. It is thus possible to estimate the proportion of those volatile fission products released from the precipitation tank both during and after the criticality accident until the sample was taken for analysis. The concentration of \(^{131}\text{I}\) in the uranium solution at 10:35 on 30 September was calculated to be \(1.17 \times 10^6\) Bq/ml from the analytical result. Also that calculated from the total number of fissions \((2.5 \times 10^{18})\) was \(1.21 \times 10^6\) Bq/ml. Accordingly, about 4% of the \(^{131}\text{I}\) should have been released from the tank. Similarly, it was estimated that the \(^{137}\text{Xe}\) and \(^{140}\text{Xe}\) amounts released were about 20% and less than 1%, respectively. A more accurate estimate of the released volatile fission products is a topic deserving further study.

**CONCLUSION**

After the JCO Criticality Accident in Tokai-mura, analytical work on the uranium solution taken from the precipitation tank was conducted to study the details of the accident. The information obtained by the analysis are summarized as follows:
1) The total reaction during the accident was evaluated to be \((2.5 \pm 0.1) \times 10^{18}\) fissions.
2) Most of the fission products were considered to be retained in the uranium solution in the precipitation tank, except for iodine and rare gases. The released fraction of \(^{131}\text{I}\) from the solution into the conversion test building was estimated to be about 4%.
3) The concentration of boron, 5.6 g-B/L in the uranium solution in the precipitation tank, was sufficient to keep the solution in a subcritical condition.

**REFERENCES**


