TECHNICAL REPORT

XMA Analysis of Undissolved Materials Observed in NSRR Short Irradiated Uranium Dioxide Fuel

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After a short irradiation of UO₂ fuels with and without SiO₂+Al₂O₃ additive in NSRR, a comparative study of the fission products (FP) dissolved in nitric acid and undissolved materials was performed. Results of the study were: (1) The additive fuel behaved similarly to non-additive fuel. (2) In both types of fuels, the undissolved materials in dried out solution were not FP but metals existing from the fuel fabrication stage. (3) The NSRR short irradiation had great influence on the shape of the undissolved components without changing the as-fabricated compositions.

KEYWORDS: XMA, undissolved material, NSRR reactor, short irradiation, radiation effects, uranium dioxide, nuclear fuels, fuel pellets, mixed oxide fuels

I. INTRODUCTION

In the past NSRR experiments, energy deposited in UO₂ fuel was evaluated by radiochemical burn-up analysis. The γ-ray energy released from radioactive materials was measured after dissolving the irradiated fuel in nitric acid (HNO₃).

In the analysis, the error band was not large, within ±5% (1). This error band, however, tended to diverge for Gd₂O₃-UO₂ or PuO₂-UO₂ as compared with UO₂ fuel, because the γ-ray energy of these dissolved fuels is masked by the energy absorption and scattering caused by additionally produced FP or undissolved materials.

Until recently, the similar situation is appeared in pellet cladding interaction (PCI) resistant fuel developed by addition of SiO₂ and Al₂O₃ into UO₂ matrix. Regarding burn-up analysis, the additive elements are considered to have same propensity to enhance the disturbance of γ-ray energy. If so, as-established procedure for past burn-up analyses will be no more useful. Therefore, it was necessary to clarify the influence of FP or undissolved materials produced additionally by the additive fuels. For this reason, a comparative study between 8x8 BWR type UO₂ fuel with and without SiO₂+Al₂O₃ addition was carried out aiming at studying the existing FP in dissolved fuel and the undissolved materials in dried out specimens through SEM (Scanning Electro Microscope)/XMA (X-ray Micro Analyzer) analyses.

The results of the present study will be available as a data base for the burn-up study of the commercial power reactor fuels with high burn-up (30~40 MWd/kg U) region.

II. EXPERIMENTAL METHOD

Two BWR type fuel rods consisting of 10% by weight enriched UO₂ with an active column length of 135 mm were prepared. The specific difference between them was the composition of Al and Si additives. The representative physical parameters are shown in Table 1. The fuel rods were loaded into the experiment capsule for single pulse irradiation. The final deposited energies through out the experiments were almost identical, i.e. 0.95 kJ/g U for S1 fuel and 0.92 kJ/g U for R1 fuel, respectively.

The configuration of the irradiation capsule

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To identify the undissolved materials, samples of 0.1 ml solution were removed from S1D and R1D, and subsequently dried in air. These specimens are hereinafter called S1DD and R1DD, respectively. The SEM observation, for material morphology, and XMA analysis, for identifying the existed undissolved materials, were performed on dried out specimens. In the latter case, a relative wave length derived from four different diffraction crystals, such as LIF, was used. The obtained relative wave length was finally converted into the absolute one in the range of 0.1~4.0 nm.

III. RESULTS AND DISCUSSION

1. FP in Dissolved Fuel

The γ-ray spectra obtained from specimens S1D and R1D were separated into the individual energy by the computer code BOB(44) and analyzed.

The results are shown in Table 2. Nine FP for S1D and eleven FP for R1D are identified. The FP in both specimens were Ce, Eu, Ba, Cs, I, Nb, Ru, La and Zr. Silver and Tl existed only in specimen R1D. Consequently, the FP detected in both specimens were similar.

### Table 2 Summary of FP measurement for dissolved fuel and result of code prediction by ORIGEN2

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Additive (S1D)</th>
<th>Additive (R1D)</th>
<th>ORIGEN2 Prediction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non-additive</td>
<td>138Ce, 141Ce, 143Ce, 144Ce, 147Eu, 153Ba, 140Ba</td>
<td>136Ce, 137Ba, 138Cs, 141Cs, 129m Te, 198m Te, 198Te</td>
<td>141Ce, 143Ce, 147Eu, 153Ba, 140Ba</td>
</tr>
<tr>
<td></td>
<td>128Cs, 127I, 129I, 131I</td>
<td>131I, 133I</td>
<td>129m Te, 198m Te, 198Te</td>
</tr>
<tr>
<td></td>
<td>95Nb, 103Ru, 106Ru</td>
<td>95Nb, 103Ru, 106Ru</td>
<td>95m Nb, 103m Nb</td>
</tr>
<tr>
<td></td>
<td>140La</td>
<td>140La</td>
<td>140La</td>
</tr>
<tr>
<td></td>
<td>90Zr</td>
<td>90Zr</td>
<td>90Zr</td>
</tr>
</tbody>
</table>

Cesium, Ru and Zr listed in the table are well known nuclides which have been observed.
in both long-term and short-term irradiated fuel. Cerium, Ba, La, I and Nb are representative nuclides in cooled short-term irradiated NSRR fuel.

The detected FP in the non-additive specimen S1D were compared with those predicted by computer code ORIGEN2. The code input was similar to experimental conditions. The result of the code prediction is also shown in Table 2. The FP predicted by code coincided well with those of the experiment.

### 2. Undissolved Materials in Dried Out Specimen of Irradiated Fuel

The dried specimens S1DD and R1DD were first examined by SEM. The results are shown in Photo. 1. The particle shapes in these specimens are mostly rhombic. The R1DD, however, has an additional spherical one.

Photo. 1 SEM images for undissolved materials from (A) S1DD and (B) R1DD in dried fuel where two arrows for rhombic particles and one for a spherical particle are the objectives of XMA analyses.

The XMA analysis was conducted to the particles identified by arrows in Photo. 1. Results for specimen S1DD having the rhombic particle are shown in Fig. 1 and Table 3. Eight metal components, i.e. U, Al, O, Zn, Fe, Pb, Na and Sn were detected. In Fig. 1, the largest peaks for Zn and Cu were from the specimen holder. Remainded peak locations with respect to Zn, however, were available to this study. The detected components were metal which might be derived either from fuel or cladding. Oxygen might be from the atmosphere.

Results on specimen R1DD having the rhombic particle are given in Table 3. It is apparent from the table that the identified material components are similar to S1DD.

Results on specimen R1DD with the spherical particle are given by Table 3. Only metal components of Pb and Zn are found. It is significant to note that they both possess a relatively low melting point, i.e. 327°C for Pb and 420°C for Zn, respectively.

Regarding the rhombic particles, on the other hand, they additionally contained high melting point metals such as Fe (m.p. = 1,539°C) together with low melting point one. Hence, it could be postulated that different melting point metal compositions affected the formation of different particle shapes when the fuel became significantly hot during irradiation.

As a complementary study, XMA analysis of aforementioned two irradiated specimens prior to being dissolved was conducted. The results are shown in Table 3. It is important to note that Al and Si in the additive fuel existed and that U, O, S, Ca and Sn were also present.
Fig. 1 Result of XMA analyses which performed to rhombic shape particle of specimen SDD indicated by arrow in Photo. 1(A); in which activity of included components are counted as a function of relative wave length of four different diffraction crystals like LIF.
Table 3 Results of XMA analysis on unirradiated/irradiated fuel pellet and undissolved material in dried out nitric acid solution

<table>
<thead>
<tr>
<th>Component</th>
<th>Irradiated</th>
<th>Unirradiated</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Non-additive SIDD</td>
<td>Additive R1DD</td>
</tr>
<tr>
<td></td>
<td>PD(^{1})</td>
<td>AD(^{2})</td>
</tr>
<tr>
<td>U</td>
<td>○ (^{1})</td>
<td>○</td>
</tr>
<tr>
<td>Al</td>
<td>× (^{4})</td>
<td>○</td>
</tr>
<tr>
<td>Si</td>
<td>○</td>
<td>○</td>
</tr>
<tr>
<td>O</td>
<td>○</td>
<td>○</td>
</tr>
<tr>
<td>S</td>
<td>○</td>
<td>×</td>
</tr>
<tr>
<td>Ca</td>
<td>○</td>
<td>×</td>
</tr>
<tr>
<td>Zn</td>
<td>×</td>
<td>○</td>
</tr>
<tr>
<td>Fe</td>
<td>×</td>
<td>○</td>
</tr>
<tr>
<td>Pb</td>
<td>×</td>
<td>○</td>
</tr>
<tr>
<td>Na</td>
<td>×</td>
<td>○</td>
</tr>
<tr>
<td>Sn</td>
<td>×</td>
<td>○</td>
</tr>
</tbody>
</table>

Note: \(^{1}\) PD: Prior to dissolution, measured at fuel pellet surface  
\(^{2}\) AD: After being dissolved  
\(^{3}\) ○: Detected  
\(^{4}\) ×: Undetected

3. Undissolved Material in Dried Out Specimens of Unirradiated Fuel

In order to determine if the revealed metallic materials originated from fuel fabrication or from irradiation, unirradiated fuels with and without additives were provided for comparison.

They had the same physical parameters as Table 1 and were dissolved in nitric acid, diluted by distilled water and dried in air. Finally, the non-irradiated dried specimens U-S1DD and U-R1DD were prepared.

The results of SEM observation are shown in Photo. 2. Morphological comparison reveals...
that there is no significant difference both specimens. Lots of cocoon-shaped particles were observed. It is noted that the shape is slightly different from irradiated specimens but not too much. No spherical particles were observed.

The lack of spherical particle existence implies that there is an influence of irradiation on the transformation of particle shape. According to NSR-77 code calculation\(^{(7)}\), the additive fuel reached a temperature of 2,200°C after 3 s of pulse irradiation. Although irradiation time was very short, the high temperature generated at that time could have much affect on the transformation of original to spherical shape. This may possibly occur the melting of any metallic materials.

The XMA analysis on specimen U-R1DD was conducted at the area indicated by rectangular frame in Photo. 2(B). The results are shown in Photo. 3 and Table 3. It is revealed from those that U, Al, Pb, Fe and Zn are the undissolved materials in the dried specimen.

The comparison of undissolved metallic materials for irradiated and unirradiated conditions shown in Table 3 indicates there is a great similarity between them, with a few exceptions. It can be concluded that NSRR irradiation gives a small change in composition of as-fabricated metal components in fuel but has a greater influence on the shape of
produced particles due principally to the higher temperature.

With respect to the influence of irradiation on additive compositions, it is clear from Table 3 that Al and Si existed in the unirradiated condition and in the irradiated one prioring to being dissolved. However, Si did not exist in dried specimen. It can be assumed that Si is either dissolved in nitric acid or not detected by XMA due to the limit of detection.

IV. CONCLUSION

Obtained results through this experiment are:

1. The FP dissolved in nitric acid solution and undissolved materials in dried samples are similar in the both additive and non additive fuels.

2. In the dried samples, rhombic and spherical shape particles existed. The particles were all metallic and derived from the fuel fabrication stage rather than FP.

3. The NSRR (Nuclear Safety Research Reactor) irradiation caused less compositional change of undissolved metal particles but had greater influence on particle shape formation.

ACKNOWLEDGMENT

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REFERENCES

Several abstracts of Japanese articles are presented in this document:

**Exposition** Current Status and Future Scope of Gamma-Ray Buildup Factor: By Research Committee on Shielding of Radiation Facilities; Build up Sub-Committee, (Received Feb. 24, '88), pp. 385~393.

**Exposition** Applications of Superconductivity to Nuclear Fuel Cycle: By Nobuyuki SASAO, Jun KUBOTA, (Received Mar. 9, '88), pp. 394~399.

**Review** Small and Medium Sized Reactors and Its Recent Foreign Response among Countries: By Kiyoaki TAKETANI, (Received Feb. 16, '88), pp. 400~409.

Concerning small and medium sized reactors, the countries concerned have been increasingly interested in their safety, public acceptance and economy etc. In this review, the development and its strategy of the concerned countries on these reactors are described depending upon the papers of the First International Seminar on Small and Medium-Sized Reactors held 1987 summer in Laussanne, informations obtained with discussions including industrial people who are designing small and medium sized reactors and already published papers. Reactor safety is classified into four safety items for pointing out the reactor safety characteristics.


Activities of Research Committee on Fuel and Materials for Fusion Reactor were summarized. The principal innovation that have been mentioned in this data are (1) the in-situ tritium breeding and the development of tritium permeation-resistant rubber, (2) the improvement of PCA, ferritic alloys and low-activation materials and (3) the wall-surface cleaning, the development of first wall coating materials and the detailed analysis of PWI elementary process.

**Letter to the Editor** Comment : “Pipe Rupture Accident on Surry Nuclear Power Plant” : By Tadat FUJIMURA, (Received Jan. 21, '88), pp. 426.

**Technical Report** Construction of In-Core Structure Test Section in HENDEL, (II), Testing Devices and Their Performance Tests: By Yoshiyuki INAGAKI, Kazuhiko KUNITOMI, Ikuo IOKA, Yasuo KONDOH, Haruyoshi HAYASHI, Yoshiaki MIYAMOTO, Hisashi KARASUDANI, Shigeru YAMAGUCHI, Received Mar. 7, '87 ; Revised June 19, '87), pp. 427~433.

An in-core structure test section (T2) in Helium Engineering Demonstration Loop (HENDEL) simulates a part of the core bottom structure with the same scale as that of a High Temperature Engineering Test Reactor (HTTR) designed in JAERI.

Testing devices, such as an inner vessel, flow regulators, region heaters and flow rate measurement blocks, were fabricated so that T2 test section could be tested under the same conditions as those of HTTR. Design problems were solved by element tests of the devices during their fabrications. Testing devices were finally confirmed to have required performances in He gas conditions of 4.0 MPa and 1,000°C through preliminary test of HENDEL operation.
In an HTGR core consisting of graphite blocks, leakage flows of the coolant gas through gaps between blocks have unfavorable effects on the core thermal hydraulics such as the increase of the block thermal stresses and fuel temperature. A seal mechanism consisting of plate-type graphite seal elements has been devised in the design of High Temperature Engineering Test Reactor to prevent the leakage flows through gaps between core support blocks.

Experiments using air and He gas were conducted to study leakage flow characteristics of this seal mechanism under various conditions of the core support block relative displacements. The pressure loss coefficients were determined from the experiments and the design criteria were found to be satisfied by the present seal mechanism. It is also found that leakage flow characteristics of a plate-type seal mechanism were very sensitive to the wedge-shaped type block displacements.

Linearization of the nonlinear differential equation which describes the motion of uranium isotopes in the enrichment by redox chromatography was attempted. It was attained by change of variables, resulting in the analytical solution. Re-expression of this solution with the original variables, which are physically meaningful, enabled us to be exactly informed of the motion of uranium isotopes in the chromatography system. Relation of the enrichment factor and the height equivalent to theoretical plate (HETP) offered by the solution was arranged to correspond to that obtained from the distillation theory.

The solution indicates the distribution of the isotopes arising from nonstationary enrichment within a finite adsorption band. Comparison of experimental values with theoretical values, which were obtained from the analytical solution, verified their good agreement.

Sensitivity analyses for mass transport model in porous media were performed by using adjoint method. The mass transport model employed is to evaluate the performance of engineered barrier of shallow land disposal, assuming that water flows through a cylinder packed with sand. In this model instantaneous sorption equilibrium between liquid and solid phases is assumed and two types of boundary conditions which represent the nuclide release from waste package, i.e. solubility-limited case and constant leaching case, are considered. From the sensitivity analysis, it was shown that the effect of longitudinal dispersion to performance measure is very small and calculated normalized sensitivity is in the order $10^{-4} \sim 10^{-3}$ around the most probable value of longitudinal dispersion coefficient. This suggests that the term of longitudinal dispersion can be removed from the original model.

In this case analytical solution is easily introduced for two boundary conditions respectively to evaluate the performance measure of the barrier system. These simplified models, in fact, give larger estimate of the nuclide release from the engineered barrier system than that calculated from the model considering the longitudinal dispersion. They are acceptable from the standpoint of conservatism of safety assessment.

Book Reviews, pp. 460~461.
