Estimation of Input Material Accounting Uncertainty With Double-Stage Homogenization in Pyroprocessing

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Pyroprocessing is a promising technology for managing spent nuclear fuel. The nuclear material accounting of feed material is a challenging issue in safeguarding pyroprocessing facilities. The input material in pyroprocessing is in a solid-state, unlike the solution state in an input accountability tank used in conventional wet-type reprocessing. To reduce the uncertainty of the input material accounting, a double-stage homogenization process is proposed in considering the process throughput, remote controllability, and remote maintenance of an engineering-scale pyroprocessing facility. This study tests two types of mixing equipment in the proposed double-stage homogenization process using surrogate materials. The expected heterogeneity and accounting uncertainty of Pu are calculated based on the surrogate test results. The heterogeneity of Pu was 0.584% obtained from Pressurized Water Reactor (PWR) spent fuel of 59 WGd/tU when the relative standard deviation of the mass ratio, tested from the surrogate powder, is 1%. The uncertainty of the Pu accounting can be lower than 1% when the uncertainty of the spent fuel mass charged into the first mixers is 2%, and the uncertainty of the first sampling mass is 5%.

Keywords: Safeguards, Pyroprocessing, Double-stage homogenization, Heterogeneity, Nuclear material accountancy, Input material accountancy

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1. Introduction

Pyroprocessing is a spent nuclear fuel recycling technology to reduce the environmental radioactivity of waste, and may have an advantage in terms of proliferation resistance because it is based on the group recovery of TRU unlike Plutonium and Uranium Extraction (PUREX) which separates plutonium only from spent fuels [1-3]. In terms of safeguards, nuclear material accounting (NMA) is relatively easy in PUREX, which is an aqueous processing and uses an Input Accountability Tank (IAT) for input accountability [4]. On the other hand, pyroprocessing uses solid-state material as the input material to electro-reduction, and input nuclear material after de-cladding is not homogeneous. Thus, samples cannot represent entire materials, resulting in an increase of nuclear material accounting uncertainty. Therefore, a homogenization method is needed to reduce the Pu accounting uncertainty in the head-end stage of pyroprocessing, and to secure representative samples. A homogenization process was originally proposed in a conceptually designed pyroprocessing facility, Reference Engineering-scale Pyroprocessing Facility (REPF) model [5, 6] in which PWR spent fuel powder from an assembly was homogenized using 500 kg mixing equipment, such as a Nauta mixer after de-cladding and low temperature oxidation. The detailed design of the mixing equipment in the REPF model was not seriously considered in the previous study, and it will likely be difficult to adapt a large sized mixer in a hot-cell in terms of remote operation and maintenance point of view.

For an engineering-scale pyroprocessing facility (about 10 to 30 tHM/year) where one option of the feed material forms in the electro-reduction process is porous pellets [7], which are fabricated from spent fuel powder ($\text{U}_3\text{O}_8$ form) oxidized at low temperature after the mechanical de-cladding of spent fuel rods. Before the pelletizing process, the head-end process uses mixers to blend spent fuel powder with a lubricant. In case that the input material form in the electro-reduction process is a porous pellet, a double-stage homogenization method was proposed in consideration of a remote control and maintenance for hot-cell operation as well as the process throughput and the number of Destructive Analysis (DA) samples. The double-stage homogenization consists of two types of homogenization equipment. The first mixer is a 75 kg capacity tumbler mixer used to blend spent fuel powder with lubricant in the head-end process where blended spent fuel powder is later pelletized. The tumbler mixer is known as a diffusive mixer, and has a simple operation for blending powder by rotating a powder container itself. A simple operation of the tumbler mixers enables the control and repair remotely even at a relatively large capacity. The second homogenization mixer is a 10 kg capacity Nauta mixer, which is known as a convective mixer that mixes powder by rotating and revolving the screw inside a cone-shaped container. The mixing performance of the Nauta mixer is superior to that of diffusive mixers such as tumbler mixers especially when mixing...
segregating powder particles [8, 9]. However, large Nauta mixers are not suitable for hot-cell operation owing to a relatively complicated operation and weight, which make them difficult to maintain and repair remotely.

The double-stage homogenization method is explained as shown in Fig. 1. Spent fuel powder oxidized at low temperature is charged into the 1st mixers of a 75 kg capacity and mixed for several hours, and then a portion of the powder can be taken from each first mixer before blending with a lubricant. This portion of powder is the first sample, and its amount can be varied with the range of several kg to obtain sufficient representativeness from the first mixer. Three samples at the kg scale are charged into the second mixer and mixed for several hours, and then multiple (three in Fig. 1) 1 g samples are taken for a DA analysis. The remaining spent fuel powder in the second mixer will be re-charged into the first mixers to blend with the lubricant. One 450 kg PWR assembly can be processed with two operations of the double-stage homogenization process. The performance of the mixers used in the double-stage homogenization process should be evaluated to determine and minimize the number of DA samples, and it is necessary to investigate how the Pu accounting uncertainty is affected by the errors caused by the double-stage homogenization, such as the mass uncertainty of charged spent fuel to the first mixers and uncertainty of first sampling mass from the first mixers, and the difference of the Pu concentration in each first mixer.

2. Research Method

The mass of nuclear material (Pu) should be accounted from spent fuel powder, in which each powder particle contains a different concentration of Pu. Thus, to estimate the Pu mass and its accounting uncertainty, the Pu sampling uncertainty (‘heterogeneity’ in homogenization) should be obtained. The Pu heterogeneity can be expressed as a function of spent fuel powder heterogeneity and the distribution of Pu concentration. As shown in Fig. 2, the powder heterogeneity is only affected by the sampling mass, the performance of sampling (homogenization) devices, and the physical characteristics of the powder particles such as the particle size, shape, and density. But the Pu concentration of each particle does not affect on particle (powder) mixing or sampling. As conclusion, the Combination of powder heterogeneity and the distribution of Pu concentration of each particle will affect on the Pu heterogeneity which is directly related to the NMA uncertainty. There are other parameters affecting the accounting uncertainty, but this study focused on ‘heterogeneity’ related to spent fuel homogenization. As well as the heterogeneity, this study considered the other errors caused by the double-stage homogenization procedure such as the spent fuel mass charged into the mixer container, the difference of the sampling mass in each container, and the difference of Pu concentration in each mixer container.
2.1 Performance Evaluation of Nauta and Tumbler Mixers

A Nauta mixer of a 10 kg capacity, and a tumbler mixer with 10 kg and 50 kg containers were designed and fabricated (see Fig. 3) to evaluate the mixing performance with metal oxide power as a surrogate material. Table 1 shows the properties of metal oxide powder, CuO and NiO used for homogenization test, and two types of metal oxide powder were charged into a container at a mass ratio of 7:3 and mixed. During 6 or 12 hours of mixing, nine samples of 1 g were taken from nine different positions of the containers at each sampling time. Samples were analyzed using Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES, Thermo Scientific iCAP 6300). The measured uncertainty of the mass ratio is shown in Fig. 4, in which the relative standard deviation (RSD) of the mass ratio from the Nauta mixer is smaller than 0.3% at an arm (screw) speed of 0.7, and all of the RSD values in the tumbler mixer are smaller than 0.8% after 3 hours of mixing, irrespective of the container capacity. This means that a scale-up of the container size does not affect the heterogeneity which can be defined as the mass uncertainty (=RSD value) of each powder mass fraction in a 1 g sample at one sigma confidence interval. The heterogeneity can also be the same meaning as the sampling uncertainty in nuclear material accountability.

2.2 Powder Heterogeneity

Because of the sample-by sample variations caused by the sample preparations for an analysis, such as dissolution, dilution, and sub-sampling, there is a high error when determining the quantitative mass of each oxide powder in the samples. Thus, instead of a quantitative determination of each powder mass, the mass ratio of CuO to NiO (U), and its uncertainty ($\sigma_U$, $U=\frac{[\text{CuO mass}]}{[\text{NiO mass}]}$) were measured using ICP-OES, as shown in Fig. 4, in order to eliminate

### Table 1. Properties of tested metal oxide powder

<table>
<thead>
<tr>
<th></th>
<th>Density (g·cc$^{-1}$)</th>
<th>Particle size</th>
<th>Mixture fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuO</td>
<td>6.3</td>
<td>325 mesh (&lt; 45 um)</td>
<td>7</td>
</tr>
<tr>
<td>NiO</td>
<td>6.67</td>
<td>325 mesh (&lt; 45 um)</td>
<td>3</td>
</tr>
</tbody>
</table>

Fig. 3. Fabricated Nauta mixer (left) and tumbler mixer (right).
the sample-by-sample variations. The variance ($\sigma^2$) of each powder mass in mixing a binary mixture is identical to Equation 1, where $\sigma_A^2 (= \sigma_B^2)$ is the variance of each powder mass in samples, $P$ is the overall mass fraction of CuO to the total mass, and $n$ is the number or mass of the sampled particles [10]. From the error propagation in Equation 2, the mass fraction uncertainty ($\sigma_{CuO} = \sigma_{NiO}$) of each powder can be calculated with known values, $\sigma_U$ and $U$ from the test results. The value of $\sigma_{CuO} (= \sigma_{NiO})$ is $8.272 \times 10^{-4}$, $1.379 \times 10^{-3}$, $1.93 \times 10^{-4}$, and $2.757 \times 10^{-4}$ in grams, and $2.76 \times 10^3$, $4.6 \times 10^3$, $6.43 \times 10^3$, and $9.19 \times 10^3$ is the number of particles for the RSDs of mass ratio of 0.3%, 0.5%, 0.7%, and 1%, respectively.

$$\sigma_A^2 = \sigma_B^2 = \frac{P(1-P)}{n}$$

(1)
A general procedure for evaluating the relative powder heterogeneity is to mix two types of powder, take a number of samples, and determine the variance of the composition. Unlike the test of a binary mixture, spent fuel powder is a multi-component mixture in which there are many different types of powder having different Pu concentrations. Thus, the uncertainty of each powder component having different mass fractions should be calculated as Equation 3 explained by R. Hogg [11], in which \( M \) is the sample mass, \( f_i \) is the overall mass fraction of component \( i \), \( \omega_i \) is the mass of a single particle of the component, and \( \bar{\omega} \) is the overall mean particle mass. The ratio of the observed (measured) variance to the expected (theoretical) variance can be expressed as the F-ratio, which can indicate how much the powder is heterogeneous. Based on the \( \sigma \) values calculated in a binary mixture test, the powder heterogeneity as a function of mass fraction is plotted in Fig. 5. It includes the powder heterogeneity (RSD, %) of homogenized powder, and the mass ratio uncertainty (\( \sigma_U \), RSD) of 0.3, 0.5, 0.7, and 1% in the CuO/NiO binary mixture test. According to the definition of ‘homogenized’ in [11], powder mixed by the Nauta and tumbler mixer is not homogenized, and the measured value to the homogenized (=ideal) value ratio can indicate how much heterogeneous the mixed powder is. The graphs in Fig. 5 were fitted with rational5fit supported by ORIGIN software for later use in the Pu heterogeneity calculation.

\[
\frac{\sigma_U}{U} = \sqrt{\frac{\sigma^2_i}{A^2} + \frac{\sigma^2_B}{B^2}} \tag{2}
\]

2.3 Distributions of Pu Concentration in Spent Fuel Powder

The distribution of Pu concentrations should be known in order to estimate the Pu mass and its uncertainty in DA samples because the Pu mass in DA samples is a product of the mass (\( m_i \)) and Pu concentrations (\( \rho_i \)) of each powder component. In order to estimate the distribution of Pu concentrations in spent fuel powder from the axial burnup profile [12] measured by gamma scans of a PWR spent fuel, the Pu distribution in a radial direction of a spent fuel rod was calculated through a RAdial power and burnup Prediction by following fissile Isotope Distribution in the pellet (RAPID) program, which was developed to predict the radial distribution of power, burn-up, and fissionable nuclide densities [13, 14]. The Pu concentrations in a radial direction were...
calculated under the assumption that the burn-up profile is symmetrical in the axial and angular directions. With this assumption, Pu concentrations in radial direction were calculated at 30 mm intervals in the axial direction of the spent fuel rod as shown in Fig. 6 (right) in which the Pu concentration at the radial center is lower than the edge because of the lower burnup at the radial center. Then the calculated Pu concentrations were summed and the cumulative mass fraction as a function of the Pu concentration was plotted as shown in Fig. 7 in which the minimum Pu concentration is about 0.7wt%, the maximum is about 4.5wt%, and about 94% of spent fuel has a Pu concentration of 1.04wt% to 2.05wt%.

2.4 Pu Heterogeneity

Based on the powder heterogeneity calculated in Sections 2.1 and 2.2, and the distribution of Pu concentrations in spent fuel in Section 2.3, the Pu heterogeneity can be estimated. In spent fuel powder with an average burn-up of 59 GWd/tU containing 1.31wt% of Pu, the Pu heterogeneity is 0.051% in the case of ideally homogenized spent fuel powder. Considering the powder heterogeneity, the estimated Pu heterogeneity increases to 0.291% with 0.5% of RSDs of mass ratio measured in mixing tests, or 0.584% of Pu heterogeneity with 1% of mass ratio RSD, as shown in Fig. 8. It can be seen that the spent powder having a Pu concentration higher than 3wt% or lower than 1wt% does not much affect the Pu heterogeneity. This is because the mass fraction of the spent fuel powder with a Pu concentration higher than 3wt% or lower than 1wt% is very low.

3. Discussion

CuO and NiO as surrogate materials were chosen to evaluate the heterogeneity of the mixers because they can be easily analyzed by ICP-OES, and have relatively high density among metal oxide materials. It is assumed the powder heterogeneity of metal oxide powder and nuclear fuel powder is same because the heterogeneity of spent nuclear fuel powder does not exist yet, even though theoretically the heterogeneity of nuclear fuel powder with higher density may be worse than metal oxide powder. Additionally, it is assumed that spent fuel powder particles oxidized at a low temperature after decladding have similar physical properties such as particle size, density, and shape except for the Pu.
concentration of each powder particle, thus spent fuel powder particles are mixed as similar as CuO and NiO mixture.

In the section 2.1 and 2.2, the powder heterogeneity was evaluated using the Nauta and tumbler mixers. In the safeguards point of view, Pu in spent fuel is the material of interest to account, thus the Pu heterogeneity should be known to estimate the Pu accounting uncertainty. From the powder heterogeneity, the Pu heterogeneity was calculated using the distribution of Pu concentration. The Pu accounting uncertainty is a function of the Pu heterogeneity, the DA analysis uncertainty, and the number of DA samples in case that the whole powder from a spent fuel assembly is homogenized in a homogenization equipment. In the double-stage homogenization, which considers the capacity of each homogenization mixer, head-end process, and the hot-cell operation, other errors due to the double-stage homogenization operation can affect on the Pu accounting uncertainty. The following section explains how to calculate the Pu accounting uncertainty from the Pu heterogeneity in the double-stage homogenization.

### 3.1 Pu Accounting Uncertainty in the Double-Stage Homogenization Process

The double-stage homogenization process for input accountancy was conceptually designed, considering the process throughput, the number of DA samples per assembly and the Pu accounting uncertainty as well as remote controllability and maintenance for hot-cell operation. While a large homogenization mixer can make an assembly-scale powder of which the Pu mass and its homogeneity can be described by a single value of the Pu mass and its uncertainty, the double-stage homogenization cannot determine the Pu mass in each first mixer, but estimate the Pu mass as a whole and its uncertainty in an assembly-wise manner. Therefore, the Pu accounting uncertainty from double-stage homogenization is affected by several parameters such as the uncertainty of the spent fuel mass ($\sigma_{Xi}$) and first sampling mass ($\sigma_{X}$), as shown in Equation 4 below, as well as the Pu concentration difference in each first mixer, the number of DA samples, the DA uncertainty, and the Pu heterogeneity.

Spent fuel powder of 75 kg is charged into three first mixers and mixed, and the same amount of the three samples, which are about 1–5 kg of spent fuel per sample, are taken from the three first mixers. Then, it repeats twice to process the whole assembly. Six first samples are charged into the second mixer, and blended. Then six DA samples of 1 g are taken and analyzed.

$$
\begin{align*}
\sum_{i=1}^{6} (\rho_i X_i (1 + \epsilon_{xi}), & \quad \epsilon_{xi} = N(0, \sigma_{x}^2) \\
\sum_{i=1}^{6} (\rho_i X_i (1 + \epsilon_{xi}), & \quad \epsilon_{xi} = N(0, \sigma_{x}^2) \\
\text{Error (\%)} = \frac{\sum_{i=1}^{3} \left( \rho_i (\epsilon_{xi} - \epsilon_{xi}) \right)}{\sum_{i=1}^{3} \rho_i} \times 100 \\
\approx \frac{\sum_{i=1}^{3} \left( \rho_i (\epsilon_{xi} - \epsilon_{xi}) \right)}{\sum_{i=1}^{3} \rho_i} \left(1 - \frac{\sum_{i=1}^{3} \rho_i \epsilon_{xi}}{\sum_{i=1}^{3} \rho_i} \right) \times 100 = \\
\frac{\sum_{i=1}^{3} (\rho_i (\epsilon_{xi} - \epsilon_{xi}))}{\sum_{i=1}^{3} \rho_i} \times 100, \\
\epsilon_{xi} - \epsilon_{xi} = N(0, \sigma_{x}^2 - \sigma_{x}^2) \tag{4}
\end{align*}
$$

$\rho_i$: Pu concentration (\%) in each container

$X_i, \epsilon_{xi}$: the mass and error (\%) of charged powder to the tumbler mixer container

$X_i, \epsilon_{xi}$: the mass and percent error (\%) of the 1st sampling

The Pu accounting uncertainty was calculated based on the Pu heterogeneity calculated in Section 2.4 and the Pu concentration difference between the 1st mixers calculated using the distribution of Pu concentrations in Fig. 7. The maximum Pu concentration difference occurs when spent fuel powder with the lowest Pu concentration is charged into a first mixer and spent fuel powder with the highest Pu concentration is charged into the other. The lowest and highest Pu concentrations in 75 kg of spent fuel powder are 0.971wt\%, and 2.022wt\%, respectively. The rest of the spent fuel powder was randomly charged into the four other
75 kg mixers using the calculated distribution of Pu concentration shown in Fig. 7. The Pu heterogeneity used in this calculation was about 0.584% calculated from 1% RSD of the mass ratio measured in the homogenization test. In addition, the DA analysis uncertainty of Isotope Dilution Mass Spectrometry (IDMS) in hot-cell condition is 0.42% [15]. The Pu accounting uncertainty with respect to the uncertainty of the spent fuel mass charged into the first mixers and first sampling mass is shown in Fig. 9, in which the Pu accounting uncertainty linearly increase with $\sigma_X$ and $\sigma_\chi$, and $\sigma_X$ affects the Pu accounting uncertainty more than $\sigma_\chi$. A Pu accounting uncertainty of lower than 1% can be accomplished with $\sigma_X$ of 2% (1.5 kg), and $\sigma_\chi$ of 5% (50 g in the case in which the first sampling mass is 1 kg), which are within the achievable error range in the hot-cell operation.

4. Conclusion

The total uncertainty with DA analysis in nuclear material accountancy is the combination of each uncertainty of mass balance, sampling uncertainty, and measurement uncertainty of DA equipment including the random and systematic uncertainties. The sampling uncertainty is commonly very high compared to the uncertainty of mass balance and measurement equipment in the non-homogenized solid-state materials. Thus, in the present study the double-stage homogenization process for an engineering-scale pyroprocessing facility was proposed to reduce the sampling uncertainty in input material accountancy. Two candidates of mixing equipment with a capability of remote operation and maintenance were tested. Based on the test result, the Pu heterogeneity was calculated in the tumbler and Nauta mixer, and the Pu accounting uncertainty in the double-stage homogenization was estimated. The Pu accounting uncertainty was lower than 1% when the uncertainty of spent fuel mass charged into the first mixers is 2%, and the uncertainty of the first sampling mass is 5%. The parameters affecting the Pu accounting uncertainty should be determined considering the Material balance when designing the safeguards system of an engineering-scale pyroprocessing facility.

As a conclusion, the double-stage homogenization process can be utilized for input material accountancy for an engineering-scale pyroprocessing facility with a relatively low Pu accounting uncertainty while ensuring the process...
throughput and remote maintenance, and minimizing the number of DA samples. Future study will include a homogenization test with surrogate powder of higher density such as SIMFUEL made with depleted uranium powder similar to spent fuel powder to confirm the effect of the powder density on the powder heterogeneity.

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