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In-line Gamma-ray Monitoring for Dissolution of Plutonium Dioxide

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A simple in-line $\gamma$-ray monitor system has been developed to elucidate the behavior of oxidative dissolution of the refractory plutonium dioxide ($\text{PuO}_2$) powder with electrogenerated $\text{Ag}^{2+}$. The system is composed of a sedimentary type glass filter, a flow cell, a Teflon tube pump and $\gamma$-ray measurement instruments. The dissolved solution was filtered to remove the powder by the glass filter, and the filtrate was transferred to the flow cell by the tube pump. At the flow cell, $\gamma$-rays of actinide nuclides such as $^{241}\text{Am}$, $^{239,241}\text{Pu}$, $^{237}\text{U}$ and/or total $\gamma$-rays were measured with MCS mode. Dissolution of several 10 g $\text{PuO}_2$ could be continuously monitored at near real time on CRTs, which provided information of the dissolution behavior of $\text{PuO}_2$ in detail.

Keywords: $\gamma$-ray, In-line Monitor, Dissolution Behavior, $\text{PuO}_2$, MCS Mode, Sedimentary Type Glass Filter, Flow Cell, Actinide Nuclides, Near Real Time

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Ag⁴⁺による電解酸化法を用いた難溶性二酸化プルトニウム（PuO₂）挙動の簡便なγ線測定によるラインモニターフを開発した。本モニターは、揮発型ガラスフィルター、フローセル、テフロンチューブポンプ、γ線測定システムから成る。プルトニウム溶解液を揮発型ガラスフィルターによりろ過した後、そのろ液をテフロンチューブポンプを用いてフローセルに移送した。そこで、含有する数つかのアクチノイド核種（例えば²⁴⁰Am、²³⁹,²⁴⁰Pu、²³⁷U）のγ線又は全γ線をMCSモードで測定した。その結果、数十gのPuO₂の詳細な溶解挙動について、連続的にしかもリアルタイムでモニタリングすることができた。
1. INTRODUCTION

Bourges et al.\textsuperscript{1, 2} performed oxidative dissolution of 300 g PuO\textsubscript{2} successfully with electrogenerated Ag\textsuperscript{2+} in HNO\textsubscript{3} solution. This method is very attractive, because it makes possible to dissolve macro amounts of the refractory PuO\textsubscript{2} with 4 to 6 M HNO\textsubscript{3} (M: mol·dm\textsuperscript{-3}) at room temperature (30±10°C). In addition, it is convenient for a subsequent process, because the method does not require HF which is corrosive for glass and stainless steel. Then, the authors have also applied it, and favorably purified the dissolved Pu solution from \textsuperscript{241}Am and Ag with mixer-settlers in the extraction system of 3 M HNO\textsubscript{3} and 30% TBP-n-dodecane\textsuperscript{3}.

In the dissolution process, it is necessary for the process control to monitor the dissolution behavior of Pu at real time. Lecomte et al.\textsuperscript{2} reported the dissolution monitor with a spectrophotometry of Pu(VI), Am(III) and Ag(II) by periodically introducing the dissolved solution into a very short quartz cell (1 mm). The method, however, was not continuous, and seems to be undesirable because the dark-color Ag\textsuperscript{2+} solution disturbs the measurements.

The alternative effective monitoring method for the dissolution is α- or γ-ray countings. The latter is capable of measuring concentration of actinide isotopes\textsuperscript{4, 5}. In this monitoring, it should be noted that the solution is separated from the fine PuO\textsubscript{2} powder to detect amounts of plutonium dissolved. In addition, the Ag\textsuperscript{2+} is so oxidative that material must be corrosion-resistant.

This report deals with a simple continuous in-line monitoring system for the oxidative dissolution process of PuO\textsubscript{2} powder by filtering the dissolved solution and measuring γ-ray emitted from actinide nuclides with multichannel scale (MCS) mode.

2. IN-LINE MONITOR SYSTEM

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2. IN-LINE MONITOR SYSTEM

Figure 1 shows a schematic diagram of the in-line γ-ray monitor system for the dissolution of PuO\textsubscript{2} with electro-
generated Ag\(^{2+}\). The system was composed of a sedimentary type glass filter, a flow cell, a Teflon tube pump and \(\gamma\)-ray measurement instruments. Continuously the dissolved solution was separated from the solid powder by the filtration, transferred to the flow cell by the pump, measured the \(\gamma\)-ray activity with the instruments and returned to the dissolver.

2.1 Sedimentary Type Glass Filter

The cross section of the sedimentary type glass filter for the heavy and fine PuO\(_2\) powder is added in Fig. 1. Most of the powder was sunk in the lower glass tube by gravity, and the rest of the powder reached to the filter was separated from the dissolved solution with the 4G glass filter (5-10 \(\mu\)m)

If particles behave the uniform motion and Reynolds number (Re) is less than 2, the sedimentation velocity of the particles (\(V_P\): cm·min\(^{-1}\)) is given by the following equation:

\[
V_P = \frac{(\rho_p - \rho_s) \cdot g \cdot D_p^2}{18 \mu}
\]

(1)

where \(D_p\): diameter of the particles, \(\rho_p\): density of the particles (11.46 g·cm\(^{-3}\) for PuO\(_2\)), \(\rho_s\): density of the solvent (1.13 g·cm\(^{-3}\) for 4 \(M\) HNO\(_3\) at 25°C), \(\mu\): viscosity of the solvent (0.99 \times 10\(^{-3}\) N·s·m\(^{-2}\) for 4 \(M\) HNO\(_3\) at 25°C)

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\(\times 10\(^{-3}\) N·s·m\(^{-2}\) for 4 \(M\) HNO\(_3\) at 25°C)\(^{6}\), \(g\): the gravitational acceleration (9.8 m·s\(^{-2}\)), and Re: \(D_p \cdot V_p \cdot \rho_s / \mu\).

In the preliminary filtration test by using CeO\(_2\) powder instead of the PuO\(_2\), the CeO\(_2\) particles passed through the 3G glass filter (20-30 \(\mu\)m) but not through the 4G filter. Assuming that \(D_p\) for the PuO\(_2\) was 10 \(\mu\)m, \(V_P\) was calculated to be 3.4 cm·min\(^{-1}\) from the equation (1) and Re was confirmed to be much less than 2.

In order to make the particles fall down in the lower glass tube, the linear flow rate of the dissolved solution by sucking with the pump must be lower than the value of \(V_P\). Since the inner diameter of the tube was 0.8 cm, the flow
rate corresponded to 2.2 cm$^3$·min$^{-1}$.

2.2 Flow Cell and Teflon Tube Pump

The detail structure of the flow cell is also shown in Fig.1. The flow cell was made of a Teflon tube (i.d.: 1.3 mm) and held in spiral shape by a variable-depth type Acryl box in a lead shield. An Acryl window (φ 10 cm x 5 mm t), through which γ-rays were measured, was located on the glove box wall at the right side of the flow cell (see Fig.1).

The pulseless Teflon tube pump was used to transfer the filtrate solution through Teflon tubes (i.d.: 1.5 or 1.3 mm) to the flow cell. The flow rate was 1.5-3 cm$^3$·min$^{-1}$ which roughly corresponded to the $V_p$ value. The flow rate as well as the direction of the flow were changable by the pump. Clogging of the filter with the PuO$_2$ powder could be eliminated by supplying the opposite flow of the solution.

2.3 Gamma-Ray Measurement Instruments

Figure 2 shows γ-ray measurement system for the monitor. The detector used was a low-energy photon high pure Ge detector (ORTEC: LO-AX-51370-20-p), which was optimum for measurement of actinide isotopes. A multichannel analyzer (MCA) system (SEIKO EG&G: 7800-8A2) was used, which was composed of a pulse height analyzer (PHA) and two multichannel scalings (MCS). If necessary, a Cu plate (2 mm t) and an Acryl plate (5 mm t) as attenuators were placed between the window and the detector.

The PHA and two MCS were simultaneously operable in on-line with a personal computor (NEC: PC-9801 VX21). Gamma-ray spectra of the filtrate sample were measured at 1000 sec intervals. On the same time, γ-rays emitted from the actinide nuclides of interest were discriminated by a quad-single channel analyzer (SCA) (ORTEC: 850). Two events of the γ-rays were continuosly inputted into the both MCS at 10 sec/channel from 1 to 4096 channels.

The respective measurements were displayed on both cathod-ray tubes (CRT) of the MCA and the personal computor.
Figure 3 shows a typical photograph of CRT of the MCA which could independently display up to 5 pictures.

3. MONITORING FOR DISSOLUTION OF PLUTONIUM DIOXIDE

Two runs of the dissolution of PuO₂ were carried out in 4 M HNO₃ at 25-28°C with oxidizing Ag⁺ electrolytically to Ag²⁺. PuO₂ samples were about 20 g of the powder which was recalcined for 2 hours at 700°C and about 80 g of the raw powder. A typical γ-ray spectrum of the dissolved solution is shown in Fig. 4. Total γ-rays, 59.5 keV of ²⁴¹Am, 129 keV of ²³⁹Pu, 149 keV of ²⁴¹Pu and 208 keV of ²³⁷U were available for the monitoring.

3.1 Dissolution of 20 g PuO₂

In the first run, total and 59.5 keV γ-rays were monitored. Figure 5 shows the dissolution curves for the both events plotted in linear (the upper graph) and semilogarithmic scales (the lower graph). The delayed time for the monitoring was about 4 min, which agreed with the arrival time of the dissolved solution to the flow cell.

Overview for the dissolution behavior was understandable in the linear scale: the dissolution of Pu started at 4 and finished at 7. Owing to about 24 % of dead time, the dissolution curves in the linear plot had a little tendency to saturate. If the dead time is corrected, each curve would become linear. Two large drop-off counts were occurred at 5 and 6 due to clogging with the PuO₂ powder. The clogging could be removed immediately from the glass filter by a temporary opposite flow of the pump. Several small drop-off counting phenomena were also observed at 8 after the dissolution finished. This was attributed to some bubbles producing in the Teflon tube owing to excess oxidative Ag²⁺, which might decompose water into a gas.

In the semilogarithmic scale, the detail behaviors in the initial process was emphasized: the dissolver was set on a magnetic stirrer at 1, the filtrate was first reached the flow cell at 2, the start point of the actual dissolution of
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Pu was clearly shown at 4.

The electrolytic current (2.5 \( A \)) began to flow at 3 and finished at 9. The start point of dissolution, however, was observed about 10 min later, which should be the delayed time (about 4 min) and probably the time (about 6 min) consuming the current for something except for the dissolution.

3.2 Dissolution of 80 g PuO\(_2\)

In the second run, 59.5-keV and 149-keV \( \gamma \)-rays were monitored for \(^{241}\text{Am}\) and \(^{241}\text{Pu}\), respectively. The flow cell was set at the farther position to avoid much dead time and the Cu and Acryl plates were placed between the window and the detector. Figure 6 shows the dissolution curves for both events plotted in linear (the upper graph) and semilogarithmic scales (the lower graph). Since the dead time (about 5\% \) was small, the dissolution curves showed linear relationship in the linear scale. No essential difference was observed between the curves for \(^{241}\text{Am}\) and \(^{241}\text{Pu}\).

The Pu behaviors are explained as follows: 80 g of the raw powder was carried into the dissolver at 1, the dissolver was set on the magnetic stirrer at 2, the first filtrate arrived to the flow cell at 3, the dissolution was over at 6, the dissolver was switched off at 8. A few fine particles were leaked through the glass filter at 5. Since the same type of another glass filter with a narrow hole edgewise was used, the leak happened several times. As well as the first run, bubbles were frequently produced at 7 until the current (10 \( A \)) was stopped at 8. The degree of the bubble production was more vigorous than that of the first run.

When the dissolver was turned on at 4, dissolution of the PuO\(_2\) was already started. This was attributed to dissolution of soluble Pu compound with only HNO\(_3\). The raw powder would contain a little Pu oxalate. Even such subtle behavior may be informed by using this monitor.
4. CONCLUSIONS

By combining a sedimentary type glass filter, a flow cell, a Teflon tube pump and γ-ray measurement instruments, an in-line γ-ray monitor system for the oxidative dissolution of PuO₂ powder was devised. The filter which was consisted of sedimentation and filtration could separate efficiently the dissolved solution from the fine PuO₂ powder. The measurement of γ-rays with MCS mode was successfully applied to the monitoring of the dissolution behavior of PuO₂.

Although this monitoring lacked corrections of dead time and back ground, the profiles displayed on the CRTs approximately corresponded to those obtained by analysis of the samples which were pipetted periodically³. Thus, the monitor system worked continuously at near real time (a time lag: about 4 min), and gave us many information on the dissolution behavior of PuO₂ in detail. In order to function at realer time, it can be achieved by minimizing the dead volume of the filter, Teflon tubes and the flow cell.

ACKNOWLEDGMENTS

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Although this monitoring lacked corrections of dead time and background, the profiles displayed on the CRTs approximately corresponded to those obtained by analysis of the samples which were pipetted periodically\(^3\). Thus, the monitor system worked continuously at near real time (a time lag: about 4 min), and gave us many information on the dissolution behavior of PuO\(_2\) in detail. In order to function at realer time, it can be achieved by minimizing the dead volume of the filter, Teflon tubes and the flow cell.

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REFERENCES


Fig. 1 Schematic diagram of the in-line γ-ray monitor system for oxidative dissolution of PuO2 with electrogeneated Ag+.
Fig. 2 Gamma-ray measurement system for the in-line monitor system.
Fig. 3 A typical photograph of CRT of the MCA.

The left pictures: the dissolution profile of 80 g PuO2 measured with MCS mode for 59.5 keV $^{241}$Am (the upper) and that for 149 keV $^{241}$Pu (the lower), the right ones: $\gamma$-ray spectrum of the flow cell measured before the dissolution (the lower), that during the dissolution (the middle) and that after the dissolution (the upper), and the comments on the CRT: the measurement conditions for the latter spectrum.
Fig. 4 A typical γ-ray spectrum of the dissolved Pu solution (attenuator: 2 mm t Cu and 5 mm t Acryl).
Fig. 5 Dissolution curves of 20 g PuO₂ plotted in linear (upper) and in semilogarithmic scales (lower) for total and 59.5-keV ($^{241}\text{Am}$) $\gamma$-rays.

1: the dissolver having 20 g PuO₂ was set on the magnetic stirrer, 2: the first filtrate was reached the flow cell, 3: the electrolytic current (2.5 A) of the dissolver began to flow, 4: the dissolution started, 5 and 6: PuO₂ particles were clogged and then removed immediately, 7: the dissolution finished, 8: some bubbles produced in the Teflon tube, 9: the electrolytic current stopped.
Fig. 6 Dissolution curves of 80 g PuO$_2$ plotted in linear (upper) and in semilogarithmic scales (lower) for 59.5-keV ($^{241}$Am) and 149-keV ($^{241}$Pu) $\gamma$-rays.

1: 80 g of PuO$_2$ was carried into the dissolver, 2: the dissolver was set on the magnetic stirrer, 3: the first filtrate arrived to the flow cell, 4: the electrolytic current (10 A) began to flow, 5: the fine particles were leaked through the glass filter, 6: the dissolution was over, 7: bubbles were frequently produced in the Teflon tube, 8: the electrolytic current stopped.