

JAERI - M
92-005

IN-LINE GAMMA-RAY MONITORING FOR
DISSOLUTION OF PLUTONIUM DIOXIDE

February 1992

Shigekazu USUDA, Satoshi SAKURAI
Sachio WAKAMATSU and Masaru HIRATA

日本原子力研究所
Japan Atomic Energy Research Institute

JAERI-Mレポートは、日本原子力研究所が不定期に公刊している研究報告書です。

入手の問合わせは、日本原子力研究所技術情報部情報資料課（〒319-11茨城県那珂郡東海村）あて、お申しこしてください。なお、このほかに財団法人原子力弘済会資料センター（〒319-11茨城県那珂郡東海村日本原子力研究所内）で複写による実費頒布をおこなっております。

JAERI-M reports are issued irregularly.

Inquiries about availability of the reports should be addressed to Information Division, Department of Technical Information, Japan Atomic Energy Research Institute, Tokai-mura, Naka-gun, Ibaraki-ken 319-11, Japan.

© Japan Atomic Energy Research Institute, 1992

編集兼発行 日本原子力研究所
印 刷 日立高速印刷株式会社

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

Shigekazu USUDA, Satoshi SAKURAI
Sachio WAKAMATSU and Masaru HIRATA⁺

Department of Fuel Safety Research
Tokai Research Establishment
Japan Atomic Energy Research Institute
Tokai-mura, Naka-gun, Ibaraki-ken

(Received January 10, 1992)

A simple in-line γ -ray monitor system has been developed to elucidate the behavior of oxidative dissolution of the refractory plutonium dioxide (PuO_2) powder with electrogenerated Ag^{2+} . The system is composed of a sedimentary type glass filter, a flow cell, a Teflon tube pump and γ -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, γ -rays of actinide nuclides such as ^{241}Am , $^{239,241}\text{Pu}$, ^{237}U and/or total γ -rays were measured with MCS mode. Dissolution of several 10 g PuO_2 could be continuously monitored at near real time on CRTs, which provided information of the dissolution behavior of PuO_2 in detail.

Keywords : γ -ray, In-line Monitor, Dissolution Behavior, PuO_2 , MCS Mode,
Sedimentary Type Glass Filter, Flow Cell, Actinide Nuclides,
Near Real Time

Notice : This work was carried out by the Japan Atomic Energy Research Institute under the entrustment by the Science and Technology Agency of Japan.

+ Department of Administrative Services, Oarai Research Establishment

二酸化プルトニウム溶解のためのインライン γ 線モニター

日本原子力研究所東海研究所燃料安全工学部

白田 重和・桜井 聡・若松 幸雄・平田 勝⁺

(1992年1月10日受理)

Ag^{2+} による電解酸化法を用いた難溶性二酸化プルトニウム (PuO_2) 挙動の簡便な γ 線測定によるインラインモニター法を開発した。本モニターは、沈降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沈降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、含有する幾つかのアクチノイド核種 (例えば ^{241}Am , $^{239, 241}\text{Pu}$, ^{237}U) 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 PuO_2 の詳細な溶解挙動について、連続的にしかもほぼリアルタイムでモニタリングすることができた。

本報告は、電源開発促進対策特別会計法に基づく科学技術庁からの受託として行った研究成果の一部である。
東海研究所：〒319-11 茨城県那珂郡東海村白方字白根2-4

+ 大洗研究所管理部

Contents

1. Introduction	1
2. In-line Monitor System	1
2.1 Sedimentary Type Glass Filter	2
2.2 Flow Cell and Teflon Tube Pump	3
2.3 Gamma-ray Measurement Instruments	3
3. Monitoring for Dissolution of Plutonium Dioxide	4
3.1 Dissolution of 20 g PuO ₂	4
3.2 Dissolution of 80 g PuO ₂	5
4. Conclusions	6
Acknowledgments	6
References	7

目 次

1. 緒 言	1
2. インラインモニターシステム	1
2.1 沈降型ガラスフィルター	2
2.2 フローセルとテフロンチューブポンプ	3
2.3 γ 線測定装置	3
3. PuO ₂ 溶解のためのモニタリング	4
3.1 20 g PuO ₂ の溶解	4
3.2 80 g PuO ₂ の溶解	5
4. 結 論	6
謝 辞	6
文 献	7

1. INTRODUCTION

Bourges et al.^{1,2} performed oxidative dissolution of 300 g PuO₂ successfully with electrogenerated Ag²⁺ in HNO₃ solution. This method is very attractive, because it makes possible to dissolve macro amounts of the refractory PuO₂ with 4 to 6 M HNO₃ ($M: \text{mol}\cdot\text{dm}^{-3}$) at room temperature ($30\pm 10^\circ\text{C}$). 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 ²⁴¹Am and Ag with mixer-settlers in the extraction system of 3 M HNO₃ and 30% TBP-n-dodecane³.

In the dissolution process, it is necessary for the process control to monitor the dissolution behavior of Pu at real time. Lecomte et al.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 Ag²⁺ 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^{4,5}. In this monitoring, it should be noted that the solution is separated from the fine PuO₂ powder to detect amounts of plutonium dissolved. In addition, the Ag²⁺ 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 PuO₂ powder by filtering the dissolved solution and measuring γ -ray emitted from actinide nuclides with multichannel scale (MCS) mode.

2. IN-LINE MONITOR SYSTEM

Figure 1 shows a schematic diagram of the in-line γ -ray monitor system for the dissolution of PuO₂ with electro-

1. INTRODUCTION

Bourges et al.^{1,2} performed oxidative dissolution of 300 g PuO₂ successfully with electrogenerated Ag²⁺ in HNO₃ solution. This method is very attractive, because it makes possible to dissolve macro amounts of the refractory PuO₂ with 4 to 6 M HNO₃ (M : mol·dm⁻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 ²⁴¹Am and Ag with mixer-settlers in the extraction system of 3 M HNO₃ and 30% TBP-n·dodecane³.

In the dissolution process, it is necessary for the process control to monitor the dissolution behavior of Pu at real time. Lecomte et al.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 Ag²⁺ 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^{4,5}. In this monitoring, it should be noted that the solution is separated from the fine PuO₂ powder to detect amounts of plutonium dissolved. In addition, the Ag²⁺ 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 PuO₂ powder by filtering the dissolved solution and measuring γ -ray emitted from actinide nuclides with multichannel scale (MCS) mode.

2. IN-LINE MONITOR SYSTEM

Figure 1 shows a schematic diagram of the in-line γ -ray monitor system for the dissolution of PuO₂ with electro-

generated Ag^{2+} . The system was composed of a sedimentary type glass filter, a flow cell, a Teflon tube pump and γ -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 γ -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 μm)⁶.

If particles behave the uniform motion and Reynolds number (Re) is less than 2, the sedimentation velocity of the particles (V_p : $\text{cm}\cdot\text{min}^{-1}$) is given by the following equation⁷:

$$V_p = (\rho_p - \rho_s) \cdot g \cdot D_p^2 / 18\mu \quad (1)$$

where D_p : diameter of the particles, ρ_p : density of the particles (11.46 $\text{g}\cdot\text{cm}^{-3}$ for PuO_2), ρ_s : density of the solvent (1.13 $\text{g}\cdot\text{cm}^{-3}$ for 4 M HNO_3 at 25°C), μ : viscosity of the solvent (0.99 $\times 10^{-3}$ $\text{N}\cdot\text{s}\cdot\text{m}^{-2}$ for 4 M HNO_3 at 25°C)⁸, g : the gravitational acceleration (9.8 $\text{m}\cdot\text{s}^{-2}$), 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 μm) but not through the 4G filter. Assuming that D_p for the PuO_2 was 10 μm , V_p was calculated to be 3.4 $\text{cm}\cdot\text{min}^{-1}$ 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 $2.2 \text{ cm}^3 \cdot \text{min}^{-1}$.

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 ($\phi 10 \text{ cm} \times 5 \text{ mm t}$), 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 $1.5\text{--}3 \text{ cm}^3 \cdot \text{min}^{-1}$ 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 computer (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 continuously 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 computer.

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 PuO_2 were carried out in 4 M HNO_3 at 25-28°C with oxidizing Ag^+ electrolytically to Ag^{2+} . PuO_2 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 ^{241}Am , 129 keV of ^{239}Pu , 149 keV of ^{241}Pu and 208 keV of ^{237}U were available for the monitoring.

3.1 Dissolution of 20 g PuO_2

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 PuO_2 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 Ag^{2+} , 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

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 PuO_2 were carried out in 4 M HNO_3 at 25-28°C with oxidizing Ag^+ electrolytically to Ag^{2+} . PuO_2 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 ^{241}Am , 129 keV of ^{239}Pu , 149 keV of ^{241}Pu and 208 keV of ^{237}U were available for the monitoring.

3.1 Dissolution of 20 g PuO_2

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 PuO_2 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 Ag^{2+} , 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

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 PuO₂

In the second run, 59.5-keV and 149-keV γ -rays were monitored for ²⁴¹Am and ²⁴¹Pu, 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 ²⁴¹Am and ²⁴¹Pu.

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 PuO₂ was already started. This was attributed to dissolution of soluble Pu compound with only HNO₃. 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 PuO_2 powder was devised. The filter which was consisted of sedimentation and filtration could separate efficiently the dissolved solution from the fine PuO_2 powder. The measurement of γ -rays with MCS mode was successfully applied to the monitoring of the dissolution behavior of PuO_2 .

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 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.

ACKNOWLEDGMENTS

The authors wish to express their appreciation to Mr. K. Obara of Analytical Chemistry Laboratory for the preparation of the sedimentary type glass filter. We are also grateful to Dr. S. Tachimori of Criticality Safety Laboratory, Dr. I. Kobayashi of Department of Fuel Safety Research, Drs. M. Kurihara and S. Fukushima of Plutonium Fuel Technology Division for their continuous interest and support of this work.

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 PuO_2 powder was devised. The filter which was consisted of sedimentation and filtration could separate efficiently the dissolved solution from the fine PuO_2 powder. The measurement of γ -rays with MCS mode was successfully applied to the monitoring of the dissolution behavior of PuO_2 .

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 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.

ACKNOWLEDGMENTS

The authors wish to express their appreciation to Mr. K. Obara of Analytical Chemistry Laboratory for the preparation of the sedimentary type glass filter. We are also grateful to Dr. S. Tachimori of Criticality Safety Laboratory, Dr. I. Kobayashi of Department of Fuel Safety Research, Drs. M. Kurihara and S. Fukushima of Plutonium Fuel Technology Division for their continuous interest and support of this work.

REFERENCES

1. J.BOURGES, C.MADIC, G.KOEHLI and M.LECOMTE, "Dissolution du Bioxyde de Plutonium en Milieu Nitrique par l'Argent(II) Electrogenere," J.Less-Common Met., 122, 303 (1986).
2. M.LECOMTE, J.BOURGES and C.MADIC, "Applications du Procede de Dissolution Oxydante de Bioxyde de Plutonium," Proc. Int. Conf. on Nuclear Fuel Reprocessing and Waste Management (RECOD 87), Paris, Aug.23-27, p.441-449 (1987).
3. S.SAKURAI, S.USUDA, N.AMI, M.HIRATA, S.WAKAMATSU, S.TACHIMORI, "Dissolution of Plutonium Dioxide by Electrolytic Oxidation Method (II), Dissolution of Macro Amounts of PuO₂ and Its Purification", J. At. Energy Soc. Jpn., to be submitted (in Japanese).
4. T.V.REBAGAY, G.A.HUFF, K.J.HOFSTETTER, "Automated Monitoring of In-Process Plutonium Concentration", Anal.Chem., 54, 8 (1982).
5. T.K.Li, "Automated In-line Measurement of Plutonium Solutions in a Plutonium Purification Process", Nucl. Technol., 55, 674 (1981).
6. "Bunseki-Kagaku Binran (ed.: the Japan Society for Analytical Chemistry)", Maruzen, Tokyo, p.1329 (1981), in Japanese.
7. "Kagaku-Kougaku Binran (ed.: the Chemical Engineering Association of Japan)", Maruzen, Tokyo, p.1056 (1978), in Japanese.
8. "Kagaku Binran (ed.: the Chemical Society of Japan)", Maruzen, Tokyo, Vol.I p.85, Vol.II, p.671, 578 (1975), in Japanese.

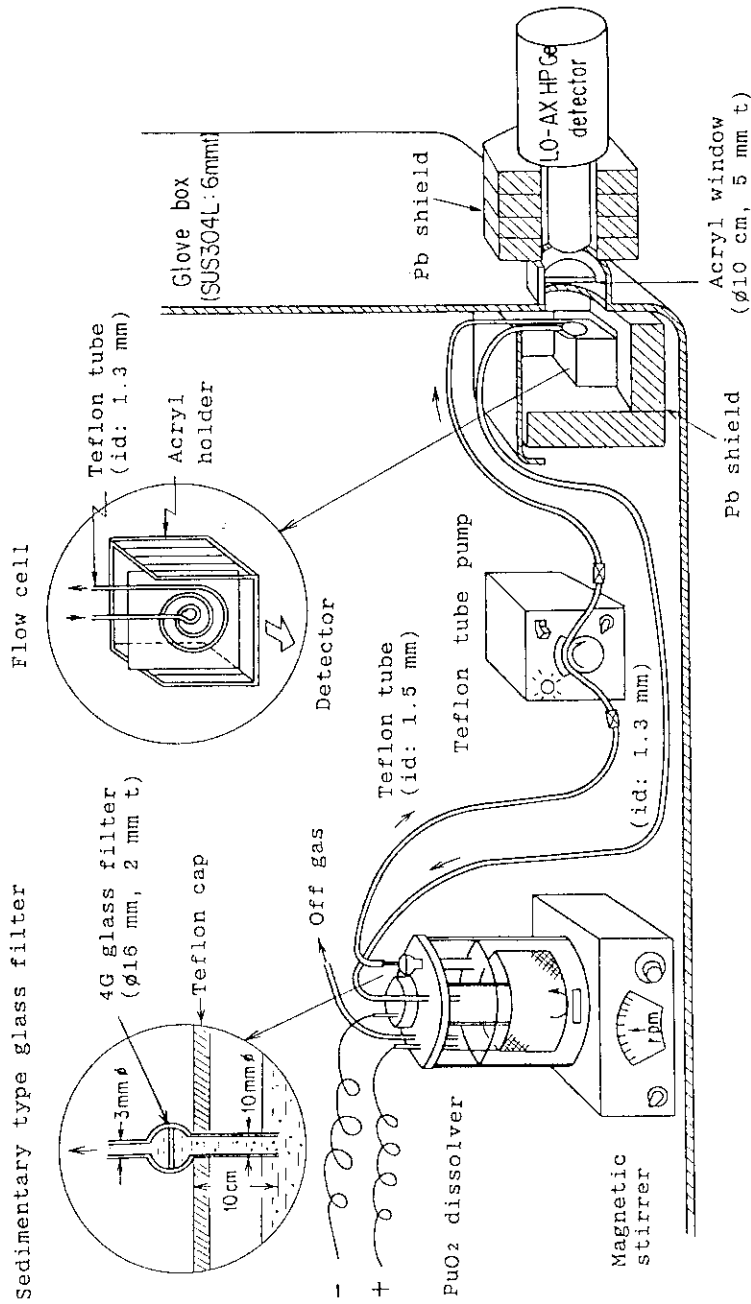


Fig.1 Schematic diagram of the in-line γ -ray monitor system for oxidative dissolution of PuO₂ with electrogenerated Ag²⁺.

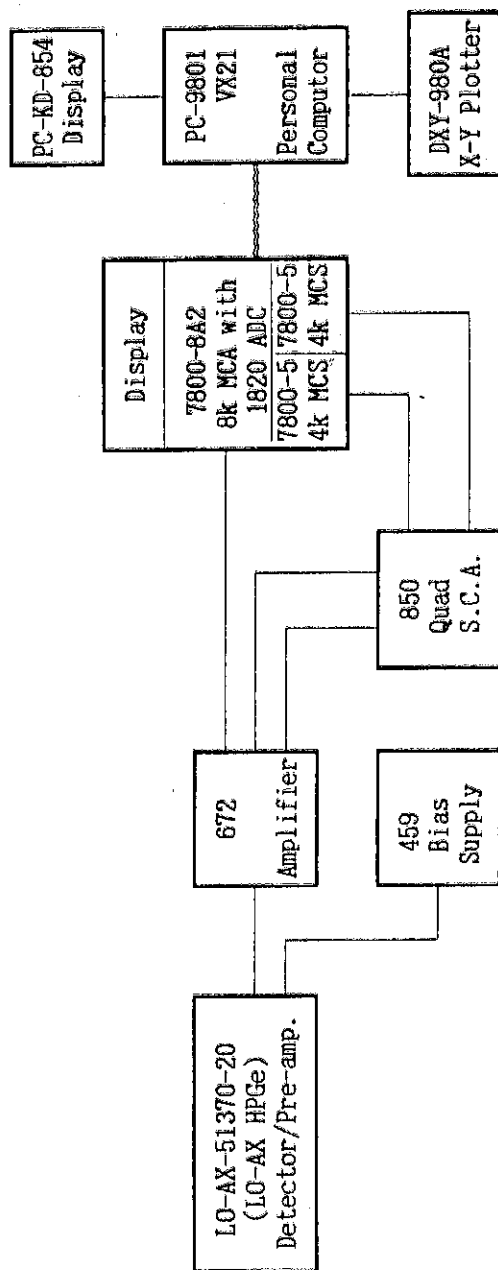


Fig.2 Gamma-ray measurement system for the in-line monitor system.

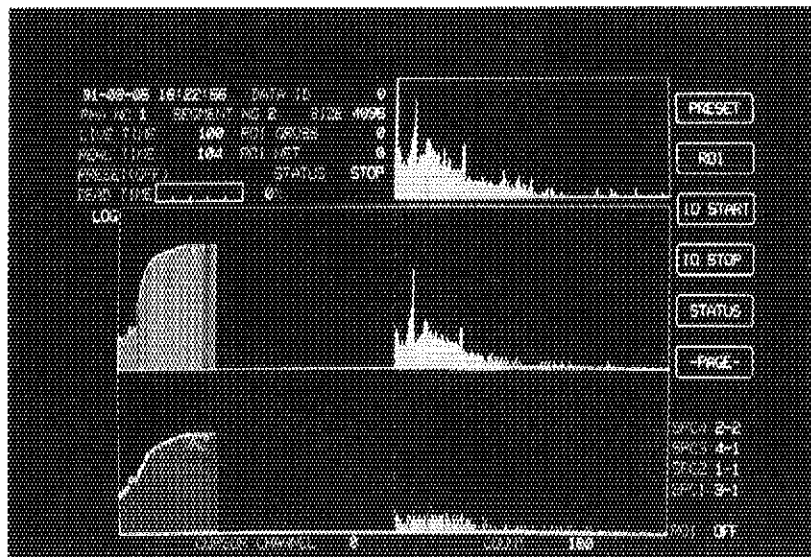


Fig.3 A typical photograph of CRT of the MCA.

The left pictures: the dissolution profile of 80 g PuO₂ measured with MCS mode for 59.5 keV ²⁴¹Am (the upper) and that for 149 keV ²⁴¹Pu (the lower), the right ones: γ -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.

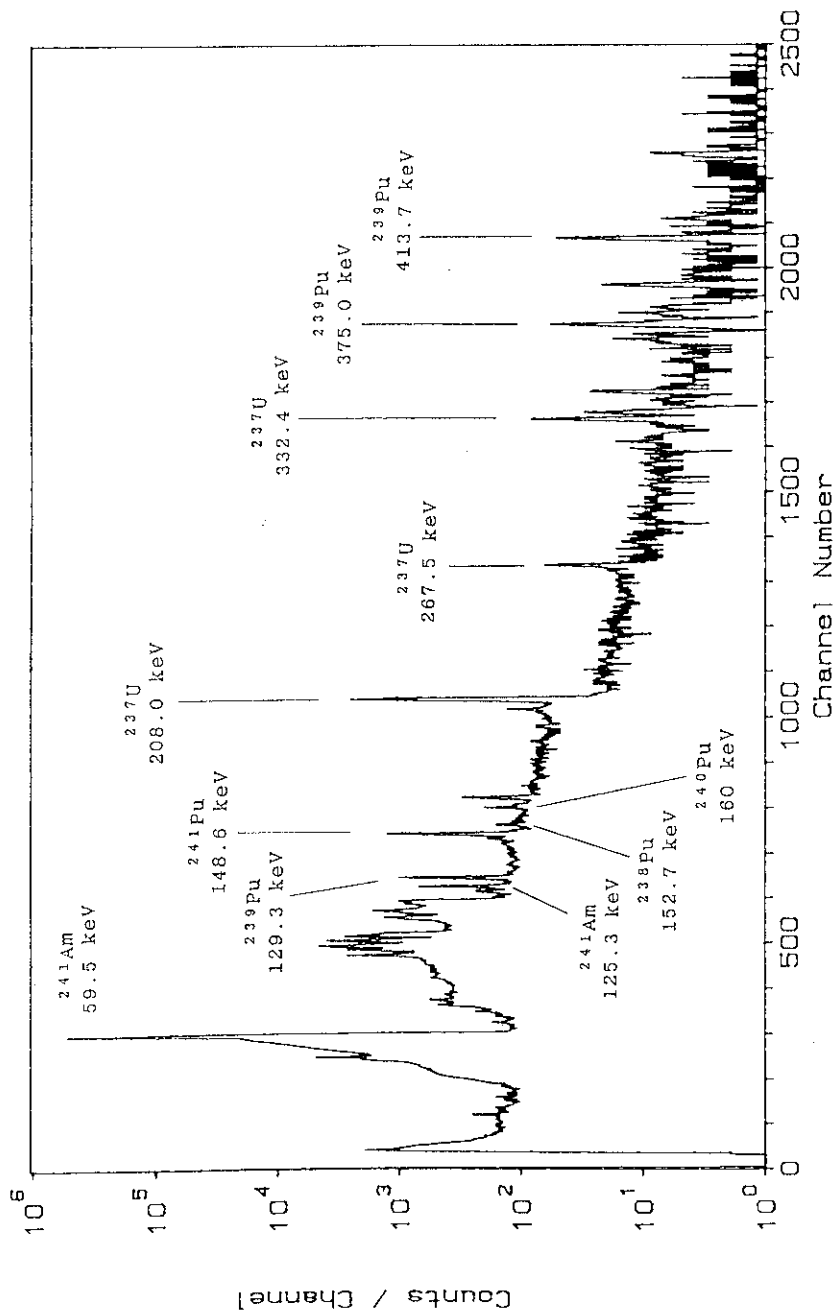


Fig.4 A typical γ -ray spectrum of the dissolved Pu solution
(attenuator: 2 mm t Cu and 5 mm t Acryl).

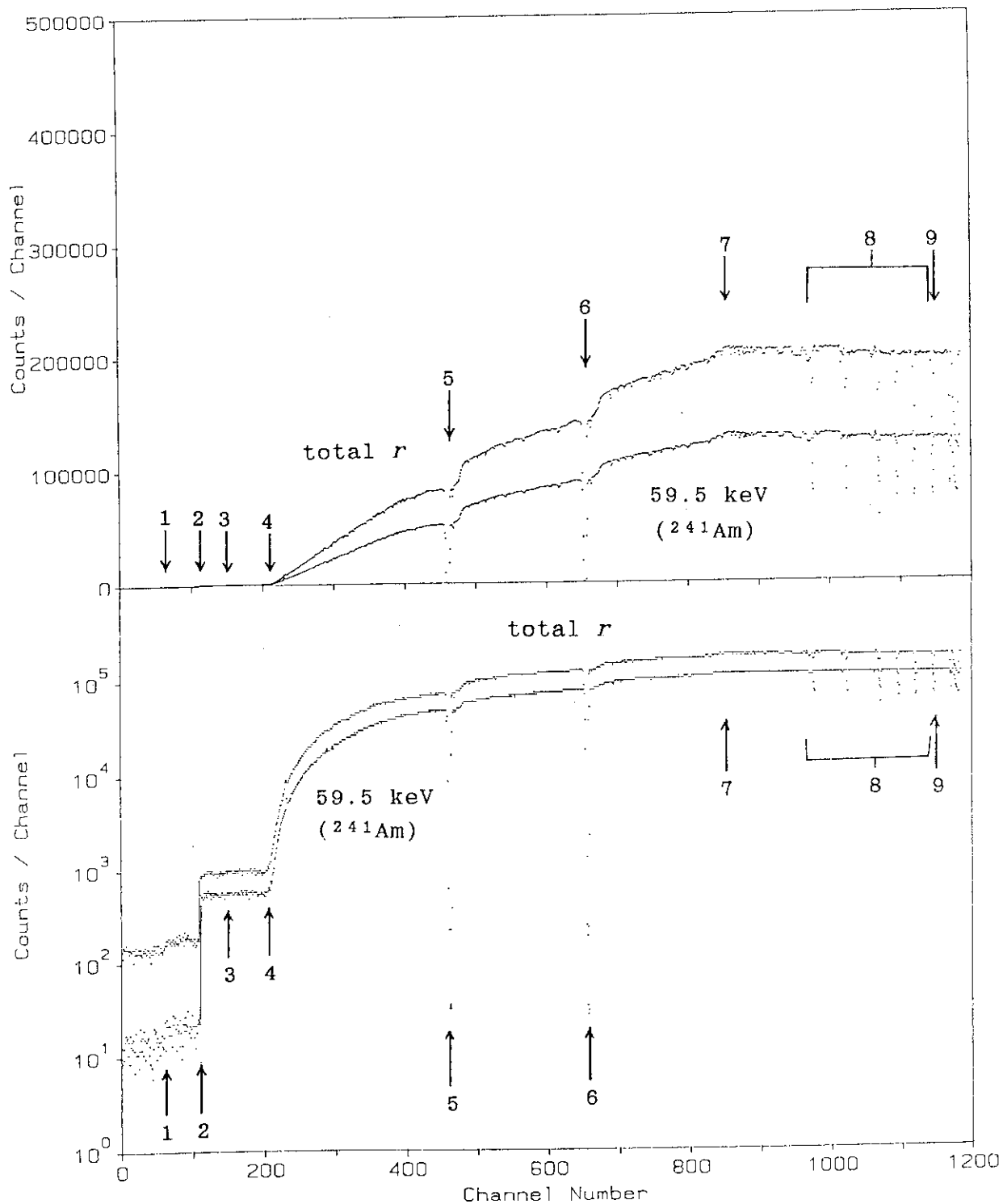


Fig.5 Dissolution curves of 20 g PuO₂ plotted in linear (upper) and in semilogarithmic scales (lower) for total and 59.5-keV (²⁴¹Am) γ -rays.

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.

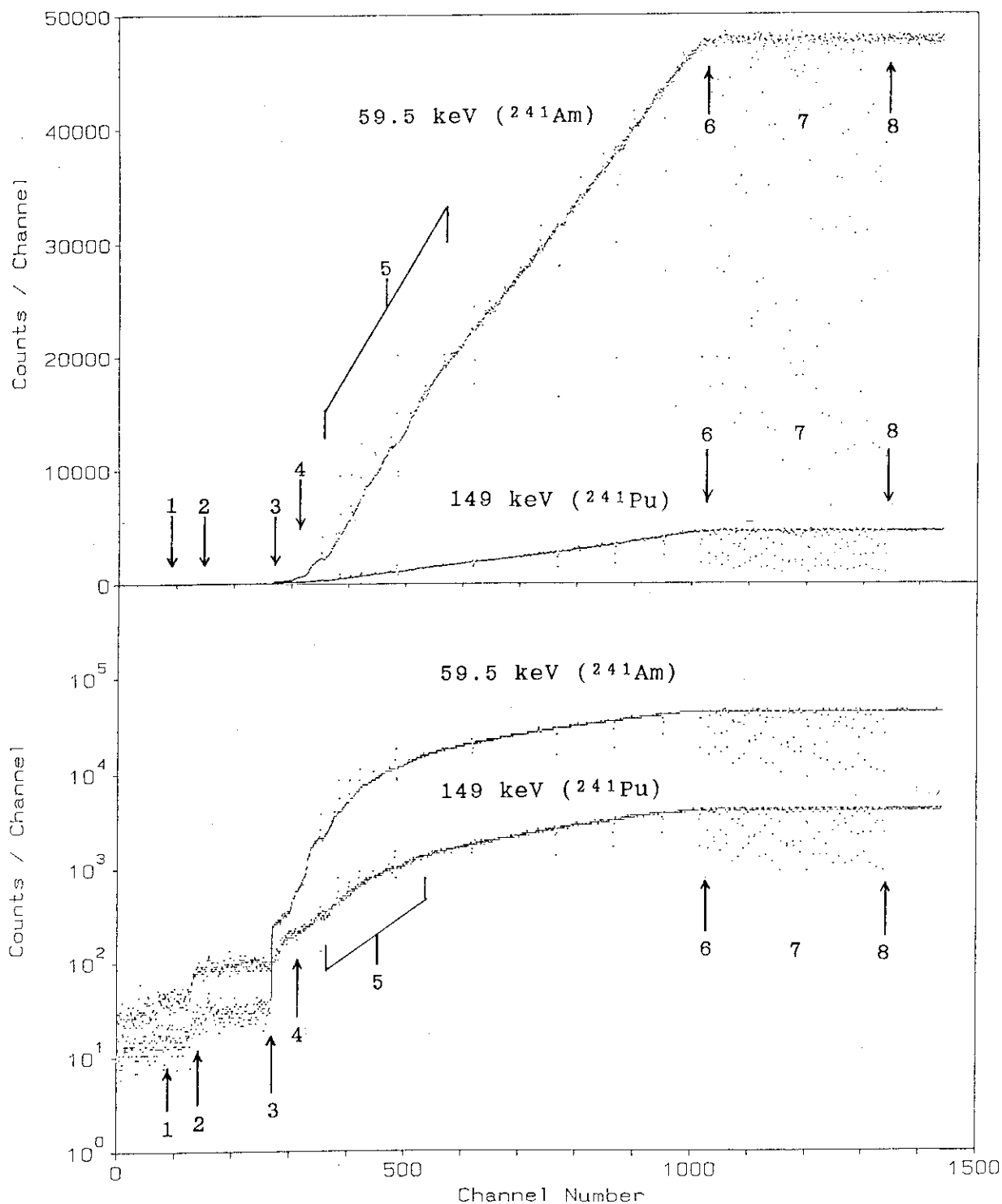


Fig.6 Dissolution curves of 80 g PuO_2 plotted in linear (upper) and in semilogarithmic scales (lower) for 59.5-keV (^{241}Am) and 149-KeV (^{241}Pu) γ -rays.

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.