



Original Article

Determination of Plutonium Present in Highly Radioactive Irradiated Fuel Solution by Spectrophotometric Method

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ABSTRACT

A simple and rapid spectrophotometric method has been developed to enable the determination of plutonium concentration in an irradiated fuel solution in the presence of all fission products. An excess of ceric ammonium nitrate solution was employed to oxidize all the valence states of plutonium to +6 oxidation state. Interference due to the presence of fission products such as ruthenium and zirconium, and corrosion products such as iron in the envisaged concentration range, as in the irradiated fuel solution, was studied in the determination of plutonium concentration by the direct spectrophotometric method. The stability of plutonium in +6 oxidation state was monitored under experimental conditions as a function of time. Results obtained are reproducible, and this method is applicable to radioactive samples resulting before the solvent extraction process during the reprocessing of fast reactor spent fuel. An analysis of the concentration of plutonium shows a relative standard deviation of <1.2% in standard as well as in simulated conditions. This reflects the fast reactor fuel composition with respect to uranium, plutonium, fission products such as ruthenium and zirconium, and corrosion products such as iron.

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1. Introduction

Mixed carbide fuel of 70% PuC and 30% UC is used as the driver fuel in the fast breeder test reactor (FBTR) at Kalpakkam, India. Spent fuel of various burn-ups from 25 GWd/t to 155 GWd/t, discharged from the FBTR with cooling periods of not less than 2 years, is reprocessed in a Compact Reprocessing of Advanced Fuel in Lead Shielded Cell (CORAL) facility. The

modified PUREX process [1–3] is followed, in which tri-n-butyl phosphate (30%) diluted with n-dodecane is employed as an extractant to recover Pu and U, leaving the bulk of fission products in a highly radioactive aqueous waste stream. A high-acid flowsheet condition [4] is adopted in order to obtain the required decontamination factor with respect to ruthenium, owing to its high yield in the fast neutron spectrum and the low cooling period of spent fuel after being discharged

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from a reactor. Samples generated at different steps of the solvent extraction process are analyzed for U, Pu, acidity, and fission product activities to understand the plant performance. Chemical methods are being followed for U analysis [5] and free acidity [6]. The alpha counting method was employed to determine the concentration of Pu in the plant samples generated at various steps during the reprocessing of spent fuel. This method is simple, rapid, and sensitive, but it requires the exact specific activity of the resultant Pu, which depends on the isotopic composition of the fissile material. As the half-life periods of ^{238}Pu ($t_{1/2} = 88$ years) and ^{240}Pu ($t_{1/2} = 6,563$ years) are less than that of ^{239}Pu ($t_{1/2} = 24,360$ years), small variations in the isotopic composition of ^{238}Pu and ^{240}Pu cause a wide range of changes in the alpha specific activity of Pu. Spent fuel from various fuel subassemblies with different isotopic compositions and burn-ups ranging from 25 GWd/t to 155 GWd/t are reprocessed in a CORAL plant. The alpha specific activity of Pu present in the irradiated fuel solution varies with respect to the burn-up and fuel subassembly. Hence, isotopic composition of the fuel material is determined first for obtaining alpha specific activity of the resultant fuel material, in order to follow the radiometric counting technique for analysis of plant samples. The increasing availability of powerful instrumental techniques such as isotopic dilution mass spectrometry [7,8], alpha spectrometry [9], and lead slowing down spectrometry has enabled the analysis of fissile content in the spent fuel discharged from a nuclear reactor. In general, isotope dilution mass spectrometry is employed for the determination of the isotopic composition of fissile material, and it involves the use of valuable reference materials and plutonium in the purest form. However, the time-consuming ion exchange chromatography technique is employed for the purification of Pu and U from fission products and minor actinides in the irradiated fuel solution for mass spectrometric studies. This step contributes considerably to high radiation exposure of the operating personnel due to the high level of fission product activities associated with spent fuel. However, the advantage of a lead slowing down spectrometer is that direct assay of isotopic fissile content in spent fuel is possible and this technique is not influenced by the intense gamma radiation background [10]. However, the above-said advanced techniques require sophisticated, expensive instruments and a skilled analyst. Hence, these techniques are employed for the analysis of a limited number of samples taken at key measurement points of the aqueous reprocessing process for the purpose of accountability. For samples with concentrations of Pu above the micromolar level, the absorption spectrophotometric method is considered to be a reliable technique for quantitative determination as well as detection of various oxidation states of Pu in the aqueous solution. The absorption spectrophotometric method reported in the literature for the determination of Pu concentration requires a suitable chromogenic agent [11] and the analyte should be in the pure form [12]. The objective of this study is to apply the direct spectrophotometric method for the determination of Pu content in the presence of major fission products such as ruthenium and zirconium, and a corrosion product (iron) from the spent fuel of a fast reactor. Hence, a tedious procedure involving the separation of Pu from complicated matrices prior to estimation is not required using

this technique. This method is very simple and less time consuming, the risk of radiation exposure is minimized, and it can be applied for analyzing radioactive samples generated in various steps of reprocessing of spent fuel.

2. Materials and methods

2.1. Chemicals and reagents

Chemicals of AR grade were used to prepare the standard solution for quantitative determination. Nitric acid (AR, Merck, Mumbai, India), potassium dichromate (AR, Merck, Mumbai, India), sodium hydroxide (AR, SD Fine Chemicals Limited, Mumbai, India), potassium hydrogen phthalate (AR, Merck, Mumbai, India), and potassium oxalate (AR, Merck, Mumbai, India) were used. Ruthenium nitrosyl trinitrate, zirconyl nitrate (AR, Lobachemie Pvt. Limited, Mumbai, India), and ferric nitrate (AR, Lobachemie Pvt. Limited, Mumbai, India) were used for the preparation of feed solution in simulated conditions. The ceric ammonium nitrate (AR, Lobachemie Pvt. Limited, Mumbai, India) required for this experiment was prepared by dissolving the required quantity in double-distilled water to the known volume. Plutonium oxide powder used in this study for the preparation of standard plutonium nitrate solution was of nuclear grade, and it was obtained by calcination of plutonium (IV) oxalate cake at 500°C after reprocessing of spent fuel discharged from the FBTR.

2.2. Instruments

A fiber-optic spectrophotometer with a wave length range of 300–1,100 nm, supplied by Ocean Optics, Dunedin, FL, USA (USB 4000 model), was used for all absorbance measurements during spectrophotometric determination of Pu concentration. An alpha scintillation counter supplied by Nucleonix (Hyderabad, India) was used for the determination of plutonium concentration by the alpha counting method.

2.3. Preparation of plutonium nitrate stock solution

All experiments with solid plutonium dioxide were performed in the glove box with extreme care. A weighed quantity of plutonium oxide was dissolved in a mixture of 11M nitric acid containing 0.1M hydrogen fluoride at 85–90°C in a 100 mL Teflon beaker. The plutonium nitrate solution was purified from americium by employing the anion exchange separation procedure using Dowex 1 × 8 resin in a nitric acid medium [13]. The concentration of Pu in the purified stock solution was determined by the redox titrimetric method using fuming perchloric acid as an oxidizing agent.

2.4. Effect of ceric ammonium nitrate concentration on the oxidation of Pu (IV) to Pu (VI)

A known volume of diluted plutonium nitrate stock solution (700 mg/L) was added to a 5 mL standard flask to get a Pu concentration of 140 mg/L. Different amounts of ceric ammonium nitrate (0.5–3.0 mL of 1M concentration) were added to the Pu already placed in a 5 mL flask. The final

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