ICP-AES Characterization of PHWR Irradiated Thoria Bundles for Fission Products

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INTRODUCTION

The current generation of Pressurized Heavy Water Reactor (PHWR) fuels have been highly optimized for the traditional PHWR fuel cycles (1-3). Thorium-based fuels have been studied for their potential applications in almost all types of reactors including Pressurized Water Reactors (PWRs), Boiling Water Reactors (BWRs), PHWRs, High Temperature Reactor (HTRs), Fast Breeder Reactors (FBRs) and Molten Salt Reactors (MSRs), though on a small scale compared to U/U-Pu fuels (4-7). With a view to address the suitability and potential advantages of a thorium-based nuclear system to perform full actinide recycling with transuranic isotopes burning, it is necessary to characterize the irradiated thoria bundles for its fission product contents.

Thoria bundles, which have been irradiated in PHWRs, are being taken up for reprocessing in the Power Reactor Thoria Reprocessing Facility (PRTRF), Bhabha Atomic Research Centre, Mumbai, India. To generate data from this thoria fuel for understanding reactor physics, analytical data such as total U and Th content, isotopic composition of generated U, individual contents of fission products and minor actinides are inevitable for understanding the irradiation history, and thereby calculation of burn-up data of thoria bundles. In this context, efforts were put towards analyzing five solutions supplied by PRTRF for their fission product and Th contents using inductively coupled plasma atomic

ABSTRACT

A methodology was optimized for the determination of fission products in irradiated thoria. Chlorinated cobalt dicarbollide (CCD) and tri-n-butyl phosphate (TBP) were employed for the separation of U and Th, respectively, for dose reduction and to avoid spectral interferences arising out of the emission rich spectra of U and Th. The tolerance level of U and Th on these analytes was found to be 100 mg L⁻¹ and 125 mg L⁻¹, respectively. Five contacts of TBP were required for preferential separation of U and Th. CCD formed a Cs⁺CCD⁻ complex through an 'ion exchange' mechanism, while TBP formed UO₂(NO₃)₂·2TBP and Th(NO₃)₄·3TBP complexes through a 'solvation' mechanism.

emission spectrometry (ICP-AES) with a glove box-adapted facility for handling radioactive samples. In view of its high sensitivity, good precision, large linear dynamic range, relative freedom from matrix effects, and its capability to provide relatively low detection limits for the simultaneous determination of common as well as rare earth impurities in different matrices, ICP-AES has been routinely used for trace metallic characterization of nuclear materials (8-15). However, the commercially available ICP emission spectrometers cannot be readily employed for the analysis of ²³⁹Pu and ²³³U based nuclear fuels due to their inadaptability to handle radiotoxic materials. Moreover, the presence of emission-rich actinides in the samples leads to erroneous results due to the spectral interference and hence, required preferential chemical separation (16-20).

EXPERIMENTAL

All of the atomic emission spectrometric studies were carried out using a Jobin-Yvon Ultima high resolution ICP-AES (Jobin Yvon, Longjumeau, France). It has the practical resolution of ≤ 0.005 nm and a spectral range of 180-800 nm. The operating conditions are chosen based on our previous reports (20) and are listed in Table I.

TABLE I
Specification and Experimental Parameters for ICP-AES Instrument

Optical Design	Czerny Turner
Grating	Holographic
Groove density	2400 / mm
Range of wavelength	120 - 800 nm
Radiofrequency	40.68 MHz
Nebulizer	Pneumatic
Ar gas flow	12 L min ⁻¹
Sample flow rate	1 mL min ⁻¹

Reagents and Standard Solutions

Rare earth elements and other common impurity standard solutions were prepared from high purity solutions (E. Merck, Darmstadt, Germany) by suitable dilutions with 0.5M HNO₃. Suprapur® (E. Merck) HNO₃ and quartz double-distilled water were used for preparing 0.5M HNO₃. The calibration plots for each analyte were obtained by using multiple standards having analyte concentrations in the 0-100 µg/mL range. This method consisted of creating an analytical method for choosing the required fission products, profiling, peak searching, and auto-attenuation of each analyte element, followed by optimization of the working parameters, calibration of

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working standards and finally, analysis of the samples in quadruplicate to establish reasonably good precision. Since the solutions received from PRTRF had a high dose radioactivity (approx. 600 mR/hr) due to the presence of ^{137}Cs , the latter was separated from these solutions using 0.1 M CCD (chlorinated cobalt dicarbollide) extractant in FS-13 (phenyl trifluoromethyl sulfone) diluent, thereby bringing down the dose of both solutions into the workable level of 20 mR/hr (21-23). Further, the major matrix elements, namely 'Th' and 'U', which are bound to cause spectral interference with the analyte detection, were separated by solvent extraction using three contacts of 30% TBP in Xylene/3M HNO_3 system (24, 25). The residual (raffinate) solution after separation of U and Th was aspirated into the plasma for the determination of potentially important fission products present in the solutions. Three solutions, which were less active

and not containing U or Th, were directly analyzed by the ICP-AES. To estimate the Th content in the dissolver and 1 AF solutions (both contain Th at % level), direct aliquots were appropriately diluted and estimated in the ICP-AES.

TBP and n-dodecane were procured from Koch-Light Laboratories, USA, and Lancaster, UK, respectively. The TBP solution was washed with 5% Na_2CO_3 to remove the acidic impurities. The FS-13 and CCD were obtained from Marshallton Research Laboratories (King, NC, USA). Figure 1 represents the structures of CCD, FS 13, and TBP used in the present investigation.

RESULTS AND DISCUSSION

Optimization of Separation Procedure

The distribution ratio values for Cs^+ (D_{Cs}) were varied as a function of aqueous feed acidity because the feed acidity plays a significant role in the extraction efficiency of dif-

ferent metal ions. In the present case, the D_{Cs} value was found to be ~ 800 from 0.01 M HNO_3 solution and this D_{Cs} value was found to decrease drastically up to 3 M HNO_3 , followed by only moderate decrease. This type of extraction profile revealed the predominance of the ion exchange mechanism shown by the following equation:

where 'aq' and 'org' represented the aqueous and organic phase, respectively. At higher feed acidity, the backward reaction is favored, therefore the D_{Cs} value reduced. 'n' is the number of CCD moieties attached to the Cs^+ ion. The equilibrium constant for the above equation can be expressed as:

$$K_{\text{ex}} = \frac{[\text{Cs}^+ \cdot n\text{CCD}^-_{\text{org}}][\text{H}^+_{\text{aq}}]^n}{[\text{Cs}^+_{\text{aq}}][\text{H}^+\text{CCD}^-_{\text{org}}]^n} \quad (\text{Eq. 2})$$

At a particular temperature and feed acidity the equation can be simplified as:

$$K'_{\text{ex}} = \frac{D_{\text{Cs}}}{[\text{H}^+\text{CCD}^-_{\text{org}}]^n} \quad (\text{Eq. 3})$$

K'_{ex} is the conditional extraction constant. After taking the logarithm of both sides of Equation 3, followed by rearrangement led to the equation as follows:

$$\log D_{\text{Cs}} = \log K'_{\text{ex}} + n \log [\text{H}^+\text{CCD}^-_{\text{org}}] \quad (\text{Eq. 4})$$

A plot of $\log D_{\text{Cs}}$ vs $\log$ CCD concentration gave a straight line with a slope ~ 1 suggesting that one CCD molecule is attached to the Cs^+ ion (Figure 2). The change in Gibb's free energy (26-27) during the extraction was evaluated as $-18.84 \text{ kJ mol}^{-1}$ revealing the spontaneity of the extraction process (Table I). This study revealed that higher feed acidity was not suitable

Fig. 1. Structure of CCD, FS 13, and TBP.

Fig. 2. The variation of D_{Cs} value as a function of (a) feed acidity and (b) concentration of CCD.

Fig. 3. Variation of D_U and D_{Th} value as a function of (a) feed acidity and (b) concentration of TBP.

for the extraction of Cs; therefore, 1 M HNO_3 was taken to serve the purpose with a $D_{Cs} \sim 200$.

Similarly, to optimize the method, the D values for Th^{4+} and UO_2^{2+} were varied as a function of aqueous feed acidity. Generally, actinides are multi-electronic systems and, therefore, have multiple lines in their emission spectra. The presence of these elements thus may lead to erroneous determination of other analytes present at the trace level due to their spectral interference. To avoid such circumstances, U and Th need to be separated from the samples without loss of other impurities. To serve the

purpose, 30% TBP in xylene was employed. The D_U and D_{Th} values were found to increase with an increase in aqueous feed acidity, followed by a plateau, suggesting the predominance of a solvation mechanism.

A similar approach was adopted to find out the metal-ligand stoichiometries for the present case. The UO_2^{2+} was found to form a 1:2 complex with TBP in xylene, whereas Th^{4+} formed a 1:3 complex (Figure 3). Both extraction processes were found to be thermodynamically favorable as suggested by the negative ΔG values. Based on the studies, it was decided that though the

TABLE II
Determination of Metal-Ligand Stoichiometry, Conditional Extraction Constants, and Change in Gibb's Free Energy for the Extraction Processes

Metal	M:L	K'_{ex}	ΔG (kJ mol ⁻¹)
UO_2^{2+}	1:2	19.1	-7.35
Th^{4+}	1:3	2.95	-2.70
Cs^+	1:1	1905	-18.84

1 M HNO_3 feed was found to be sufficient for the selective and efficient removal of Cs^+ , the feed acidity was to be readjusted to 3 M HNO_3 for the selective separation of U and Th.

Evaluation of Analytical Performance for the Considered Analytical Lines in ICP-AES

Before analyzing the actual samples, it was necessary to choose the analytical lines of the elements, which shows the desired analytical performance such as lower detection limits, higher sensitivity, and good precision. For the present investigation, the Ba 455.403 nm, Ce 413.765 nm, Eu 420.505 nm, Gd 379.639 nm, La 408.671 nm, Mo 202.030 nm, Nd 401.225 nm, Pr 414.311 nm, Sm 359.262 nm, Sr 407.771 nm, Y 371.029 nm, Th 401.913 nm, and U 385.958 nm analytical lines were chosen for their determination. The slope values for the calibration curves were determined as the sensitivity of the analytical lines. The concentration corresponding to the intensity equivalent to the blank + three times the relative standard deviation was evaluated as the detection limits for the analytes using the

mentioned lines. The % RSD values were found to be well below 5% revealing the reproducibility of the results due to the highly stable excitation source. The detection limits for all these analytical lines were found to be below 0.1 mg L⁻¹, while the sensitivity values were found to be more than E+02. Table III summarizes the analytical performance of the emission lines of the different analytes.

Evaluation of Number of Contacts

In optimizing the separation process, it is required to know the number of contacts of TBP-xylene required to reduce the U and Th concentration below a certain level (U: 100 mg L⁻¹, Th: 125 mg L⁻¹) to avoid spectral interference. Obviously, the number of steps depends on the initial concentration of U and Th. The initial concentrations for Th and U were chosen as ~ 25000 mg L⁻¹ and 1000 mg L⁻¹, respectively. It was observed that only after five contacts, the Th concentration on the raffinate became less than the tolerance level, while for U after two contacts the same can be achieved. Therefore, based on this study, five contacts were chosen for the simultaneous removal of U and Th from the analytes even at the trace level. Figure 4 shows the concentration of U and Th after each contact of TBP-xylene.

Determination of the Analytes in Dissolver Solutions of PHWR Irradiated Thoria

Five different samples (named as dissolver, 1CP, 1AF, UST1, and UST2) of dissolver solution, generated from PHWR irradiated thoria bundles, were analyzed using the following scheme as optimized earlier (Figure 5). The dissolver solution is the solution obtained after dissolving the irradiated thoria fuel assembly in HF-HNO₃ mixture. 1CP, 1AF, UST1, and UST2 refer either to different positions of irradiation per-

Table III
Analytical Performance of the Emission Lines of Different Analytes

Element	Analytical Lines (nm)	Detection Limits (mg L ⁻¹)	Sensitivity (Counts mg ⁻¹ L)	RSD (%)
Ba	455.403	0.04	1.03E+04	1.95
Ce	413.765	0.1	9.90E+02	2.94
Eu	420.505	0.07	7.36E+02	1.18
Gd	379.639	0.08	1.11E+03	0.88
La	408.671	0.09	9.67E+02	3.09
Mo	202.03	0.06	1.13E+03	4.73
Nd	401.225	0.07	9.55E+02	0.44
Pr	414.311	0.05	9.47E+02	2.1
Sm	359.262	0.07	9.14E+02	1.98
Sr	407.771	0.05	9.84E+03	2.48
Y	371.029	0.04	1.15E+04	0.23
Th	401.913	0.07	2.45E+03	3.39
U	385.958	0.1	1.17E+03	2.74

Fig. 4. Concentration of U and Th in the raffinate after each contact of TBP-xylene.

taining to a different neutron flux in the reactor, or it can be at different times of irradiation. The exact source cannot be revealed due to the confidential nature.

The very high gamma dose of the samples was reduced by preferential separation of ¹³⁷Cs by 0.1 M CCD in FS 13 from 1 M HNO₃ feed acidity. Then the sample acidity was adjusted to 3 M HNO₃ for preferential separation of U and Th using 30% TBP in xylene. Table IV

summarizes the analytical results obtained. The method was validated using synthetic samples. Since standard reference materials for such radioactive origin is not available commercially in national or international levels, a synthetic sample is one of the few choices to validate the method. Since these samples involve high level of radioactivity, other suitable analytical techniques for the determination of such multi-elements in one

stretch is practically impossible. The Th and U contents were determined by stripping the organic phase with 5% Na₂CO₃ and feeding the same into the plasma. A 1CP solution was found to contain Ce and Gd along with Th and U, while the samples identified as dissolver and 1AF contained all the specified analytes. UST1 and UST2 samples

were found to contain Ce, Gd, Nd, Pr, Sm, along with U and Th. The analytical data obtained from these studies revealed that the Nd and La concentration values, which form the basis for computing burn-up data of the fuel bundles, were in close agreement with those obtained by the ID-TIMS technique.

CONCLUSION

An ICP-AES based method was developed for the determination of fission products in the dissolver solutions originating from irradiated thorium bundles from PHWR origin. In the first step, the ¹³⁷Cs, which was responsible for the major gamma dose of the samples, was removed from 1 M HNO₃ using 0.1 M CCD in FS 13. In the second step to avoid their spectral interference, U and Th were removed from the samples using TBP-xylene. The ion exchange mechanism was found to be predominating with metal-ligand stoichiometry of 1:1 for Cs with CCD, whereas the solvation mechanism was found to be operative with metal-ligand stoichiometry of 1:2 and 1:3 for UO₂²⁺ and Th⁴⁺, respectively. All the

extraction processes were found to be thermodynamically favorable as revealed from the negative ΔG values. The U and Th concentrations were determined by stripping the loaded TBP-xylene using Na₂CO₃ solution, followed by feeding into the plasma.

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Fig. 5. Scheme for analysis of dissolver solutions from irradiated thorium bundles from PHWR.

TABLE IV
Analytical Data Obtained by ICP-AES Analysis of Dissolver Solution

Elements	Synthetic Samples Actual Amount (mg L ⁻¹)	Amount Estimated (mg L ⁻¹)	Dissolver (mg L ⁻¹)	1CP (mg L ⁻¹)	1AF (mg L ⁻¹)	UST1 (mg L ⁻¹)	UST2 (mg L ⁻¹)
Ba	5	4.6±0.2	3.9±0.04	< 0.1	5.7±0.6	< 0.1	< 0.1
Ce	3	3.1±0.1	6.4±0.1	0.16±0.003	9.0±0.3	0.36±0.07	0.84±0.04
Eu	0.2	0.17±0.01	0.2±0.04	< 0.1	0.28±0.01	< 0.1	< 0.1
Gd	0.5	0.52±0.03	0.12±0.05	0.44±0.08	0.32±0.05	1.4±0.04	3.2±0.06
La	2	1.8±0.2	3.3±0.03	< 0.1	4.8±0.04	< 0.1	< 0.1
Mo	2	2.0±0.2	2.5±0.5	< 0.1	9.4±0.4	0.32±0.02	< 0.1
Nd	5	5.1±0.4	9.6±0.2	< 0.1	15±0.7	< 0.1	0.24±0.03
Pr	2	1.9±0.1	3.0±0.1	< 0.1	4.9±0.09	0.24±0.1	0.24±0.1
Sm	1	1.08±0.08	1.8±0.05	< 0.1	2.6±0.1	0.8±0.05	1.6±0.02
Sr	2	2.07±0.08	3.4±0.06	< 0.1	5.1±0.1	< 0.1	< 0.1
Y	2	1.92±0.05	1.8±0.1	< 0.1	2.9±0.1	< 0.1	< 0.1
Th	5	4.8±0.2	12350±180	70±1	23450±700	16±0.8	9.0±0.7
U	10	9.5±0.6	133.21±0.07	109.8±0.3	167.6±0.8	300.6±0.6	600±2

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