



Validation and improvement of curium radiochronometry to determine the model discharge date of spent nuclear fuels

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Abstract

This study validates and improves the Cm radiochronometry method developed to determine the model discharge date of nuclear spent fuels based on a three isotopes system, specifically the $^{244}\text{Cm}/^{246}\text{Cm}$ and $^{244}\text{Cm}/^{245}\text{Cm}$ ratios change since discharge time. Six spent fuel samples with continuous irradiation histories were used. After Cm separation from the matrix, the Cm isotopes were measured by accelerator mass spectrometry using one of the samples as internal standard for normalization. The mean average deviation from the known fuel discharge date improved from 3.3 ± 2.8 to 2.7 ± 2.6 yr when using spent fuel with continuous irradiation.

Keywords Curium isotopes · Radiochronometry · Fuel discharge date · Nuclear forensics · Accelerator mass spectrometry

Introduction

Nuclear forensics aims to support national and international law enforcement investigations into the illicit and malicious use of nuclear materials [1]. A wide range of nuclear forensics methods are applied to determine the origin and intended use of either a stolen or found radioactive material [2–4]. Developing and improving nuclear forensic techniques is important to deter against the harmful use of nuclear materials and be better prepared to support investigations when nuclear materials are found outside of regulatory control.

Radiochronometry is an important technique in nuclear forensics to determine model ages of nuclear and radioactive materials. Model ages are usually determined by measuring the amounts of a parent isotope and its progeny in a sample of the material and then, by calculating the time since purification and analysis using the Bateman equation. A number of progeny and parent isotope pairs have been used as radiochronometers such as $^{230}\text{Th}/^{234}\text{U}$ and $^{231}\text{Pa}/^{235}\text{U}$ for uranium materials, $^{234}\text{U}/^{238}\text{Pu}$, $^{235}\text{U}/^{239}\text{Pu}$,

$^{236}\text{U}/^{240}\text{Pu}$, and $^{241}\text{Am}/^{241}\text{Pu}$ for Pu materials [2, 3], as well as $^{60}\text{Ni}/^{60}\text{Co}$ and $^{137}\text{Ba}/^{137}\text{Cs}$ for Co [5] and Cs [6] radioactive sources, respectively. However, when estimating model ages, two key assumptions are made: the progeny isotope was completely removed during purification and both elements were contained in a closed system following processing [7].

Along with the mentioned assumptions, the measurement of both isotopes should be as precise and accurate as possible to correctly determine a material's model separation or discharge date [8, 9]. A precise and accurate determination of the parent isotope is usually easier to achieve than for the progeny isotope because the progeny isotope is typically present at trace level in the material. Furthermore, a chemical yield tracer is needed for most radiochronometers to correct for recovery losses during radiochemical separations. The recovery tracer can contain the progeny and render the measurement less accurate. Consequently, complex radiochemical separations, very pure or well characterized tracers, representative method blanks, ultra-sensitive measurement techniques, and specialized installations, where highly radioactive materials can be handled and a low laboratory background is maintained to reduce the risk of contamination, are needed. Measurements are usually made with radiometric and mass spectrometry techniques such as gamma spectrometry, alpha spectrometry, and inductively coupled plasma mass spectrometry [10], or a combination of the above

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techniques. Finally, the use of multiple radiochronometers is recommended when possible to add confidence in the determination of the model age [3].

The model discharge date of a spent nuclear fuel is particularly challenging to determine with high accuracy because the parent/progeny ratio used for the radiochronometry model can be affected by fission reactions, neutron captures, and radioactive decay of other isotopes. For this reason, most of forensics investigations on nuclear fuels focus on determining the ^{235}U enrichment and type of reactor used based on selected isotopic ratios (e.g. U and Pu) [2, 10, 11]. Only a few studies have investigated the use of isotopic radiochronometers such as $^{241}\text{Pu}/^{241}\text{Am}$, $^{242}\text{Pu}/^{240}\text{Pu}$ vs $^{241}\text{Pu}/^{239}\text{Pu}$, $^{152}\text{Eu}/^{154}\text{Eu}$, and $^{88}\text{Sr}/^{90}\text{Sr}$ to determine the model discharge date of a spent nuclear fuel [12–15]. We recently studied the use of Cm isotopic ratios as a new method to determine the discharge age of spent nuclear fuels [16]. This was a new type of application for Cm isotopes because Cm isotopes in spent nuclear fuels are mainly studied for their toxicity in the context of nuclear wastes [17–19].

The new Cm radiochronometry technique we developed to determine the model discharge date of a spent nuclear fuel is based on three Cm isotopes (^{244}Cm , ^{245}Cm , and ^{246}Cm) [16]. In a nuclear reactor, ^{244}Cm is mainly formed by neutron capture from ^{243}Cm and ^{243}Am ($^{243}\text{Cm}(\text{n}, \gamma)^{244}\text{Cm}$ and $^{243}\text{Am}(\text{n}, \gamma)^{244}\text{Cm}$). Then, the higher mass Cm isotopes (^{245}Cm to ^{250}Cm) are also mainly produced by neutron capture reactions from a lower mass Cm isotope ($^{24x}\text{Cm}(\text{n}, \gamma)^{24(x+1)}\text{Cm}$) and the total fluence determines the proportion of Cm isotopes formed [20]. Only a very small proportion of the Cm isotopes is formed by the decay of some Bk and Cf isotopes. A nuclear fuel irradiated for a longer time will contain a greater proportion of higher-mass Cm isotopes. The ratio $^{245}\text{Cm}/^{246}\text{Cm}$ does not change much after irradiation as these two isotopes of Cm have relatively long half-lives ($t_{1/2} = 8,250 \pm 70$ yr and $4,723 \pm 27$ yr, respectively [21]). On the other hand, the $^{244}\text{Cm}/^{246}\text{Cm}$ ratio decreases significantly with time due to the shorter ^{244}Cm half-life of 18.11 ± 0.03 yr [21]. The relation between $^{244}\text{Cm}/^{246}\text{Cm}$ and $^{245}\text{Cm}/^{246}\text{Cm}$ ratios at end of irradiation (time since discharge from the reactor) seemed to be universal based on previous results [16]. The relation can be used as a reference curve to calculate the $^{244}\text{Cm}/^{246}\text{Cm}$ ratio at end of irradiation. To determine the model discharge date of a spent nuclear fuel sample using the Bateman equation, the current ratio of $^{244}\text{Cm}/^{246}\text{Cm}$ is determined by mass spectrometry and the $^{244}\text{Cm}/^{246}\text{Cm}$ ratio at end of irradiation is calculated using the reference curve of $^{244}\text{Cm}/^{246}\text{Cm}$ ratio as a function of $^{245}\text{Cm}/^{246}\text{Cm}$ ratio [16]. Like other single element radiochronometers, the main advantages of this method are that no tracer is needed, the Cm isotopes have the same behavior

in the environment (the system does not have to be closed), and the method can work on a nuclear material where the progeny did not have to be separated from the parent at end of irradiation. In the case of reprocessed fuels, where Cm removal could have been incomplete following the first irradiation, the model age would be a composite of both times since irradiation.

The $^{244}\text{Cm}/^{246}\text{Cm}$ ratio as a function of the $^{245}\text{Cm}/^{246}\text{Cm}$ ratio relation obtained in the initial work had a correlation that was good ($R^2 = 0.935$) but that could be improved [16]. As a result, the maximum uncertainty using this radiochronometer for age-dating was ± 5 years [16]. The discontinuous irradiation of the fuel samples used for the initial study could explain the rather low accuracy. Indeed, the fuel samples available for the initial study were often removed and put back in the reactor over the years, resulting in a significant decay of ^{244}Cm . The $^{244}\text{Cm}/^{246}\text{Cm}$ value at end of irradiation was potentially lower than it would have been for fuels with the same discharge date but continuous irradiation. This could be the source of a systematic deviation from the expected correlation and therefore lowered the precision of the model ages. A lower than expected $^{244}\text{Cm}/^{246}\text{Cm}$ ratio would result in an overestimated discharge age, thus the Cm model discharge date can be interpreted as the earliest possible discharge date.

For this current work we improved the $^{244}\text{Cm}/^{246}\text{Cm}$ vs $^{245}\text{Cm}/^{246}\text{Cm}$ ratios curve (reference curve) by adding six uranium fuel samples that had been continuously irradiated in CANDU power reactors. The fuel samples were dissolved and Cm was radiochemically purified and determined by accelerator mass spectrometry (AMS). The precision of the AMS measurement was improved using one sample as an external normalization standard. The fuel age was calculated using the Cm radiochronometry technique previously developed [16].

Experimental

Instruments

Accelerator mass spectrometry

Curium isotope measurements of six samples and two blanks (E series in Tables 1 and 2) were performed with the compact, low-energy AMS system MILEA at ETH Zurich, Switzerland. The MILEA system was installed at ETH Zurich in 2018, and since 2019 it has been routinely used for actinide analyses. A detailed description of the MILEA system and its setup for actinides is presented elsewhere [22], and here only a brief description of the instrumental

Table 1 Fuel history

Sample ID	Irradiation time (yr)	Average discharge burnup (MWh(kgU) ⁻¹)	Time between discharge and analysis (yr)
E-1	Unknown	186	30.13
E-2	2.1	187	14.04
E-3	1.3	234	13.58
E-4	1.7	184	7.92
E-5	2.2	230	8.25
E-6	1.6	203	11.86

Table 2 Average counting rates measured by AMS of ²⁴⁴Cm, ²⁴⁵Cm, and ²⁴⁶Cm in samples and blanks

Fuel ID	Blank corrected counting rate CR _{net} (cps)		
	²⁴⁴ Cm ± 1σ	²⁴⁵ Cm ± 1σ	²⁴⁶ Cm ± 1σ
E-1	210 ± 1	5.71 ± 0.05	0.65 ± 0.02
E-2	500 ± 3	7.25 ± 0.05	0.84 ± 0.02
E-3	52.6 ± 0.5	0.90 ± 0.02	0.12 ± 0.01
E-4	697 ± 4	8.65 ± 0.06	0.95 ± 0.02
E-5	89.8 ± 0.5	1.30 ± 0.02	0.19 ± 0.01
E-6	64.5 ± 0.5	0.93 ± 0.02	0.10 ± 0.01
	Counting rate (cps)		
Blanks (n=2)	0.5 ± 0.4	0.006 ± 0.006	0.003 ± 0.003

setup for Cm-isotope measurements is presented. ^xCm isotopes (x = 244, 245, 246) were sequentially injected into the accelerator using the slow bouncing system. In total, the samples were analyzed for 12 passes, with one pass consisting of three repetitions of the following sequence: ²⁴⁴Cm (10 s), ²⁴⁵Cm (15 s), and ²⁴⁶Cm (30 s). Isotopic ratios of ²⁴⁴Cm/²⁴⁶Cm and ²⁴⁵Cm/²⁴⁶Cm were calculated from the method blanks corrected counting rates on each mass. To construct the reference curve, the isotopic ratios were decay-corrected using the known decay time between discharge and analysis of the samples (Table 1).

The fact that no certified standard material exists for ²⁴⁴Cm/²⁴⁶Cm and ²⁴⁵Cm/²⁴⁶Cm ratios complicates comparability with our previous AMS results [16]. For example, different machine tuning and ion beam transport may have a systematic effect on the measured isotopic ratios. Such effects are commonly known and generally eliminated by normalizing the measured ratios to an internal or external standard material with known isotopic ratios, however there is no available Cm isotopic standard. To circumvent this problem we decided to prepare two AMS targets using sample E-4 from this study as an external standard. In a separate AMS run, the samples from our previous study were measured again on the MILEA system together with the two newly prepared E-4 samples and with two blanks.

By comparing the measured isotopic ratios for sample E-4 from both runs, the isotopic ratios of the initial samples were re-normalized relative to the new set of samples. The underlying isotopic ratios of all samples are reported relative to the measured isotopic ratios of sample E-4. Future analyses of spent nuclear fuel samples for Cm radiochronometry will thus also require the analysis of sample E-4 to allow the normalization of the measured isotopic ratios relative to the ²⁴⁴Cm/²⁴⁶Cm and ²⁴⁵Cm/²⁴⁶Cm ratios of sample E-4.

Gamma spectrometer

A coaxial high-purity germanium (HPGe) detector shielded with 10 cm of lead (AMETEK/ORTEC Inc., Oak Ridge, TN, USA) was used to confirm the removal of the lanthanides before the separation of Cm from Am.

Alpha spectrometer

An Octete Plus® alpha spectrometer with eight 450 mm² ULTRA-AS ion-implanted silicon detectors (AMETEK/ORTEC Inc., Oak Ridge, TN, USA) was used to confirm the separation of Cm from Am and to estimate the amount of Cm isotopes in the samples prior to the preparation of the AMS targets.

Fuel description and irradiation history

Six natural UO₂ fuel elements from CANDU commercial power reactors with continuous irradiation histories were selected for this work (see Table 1). The fuel samples had burnups between 190 and 230 MWh(kgU)⁻¹ and were discharged from the reactor between 1992 and 2014. All samples were sectioned at the same distance from the reference end of the fuel element (fuel pin).

Curium purification

Curium isotopes were separated from the spent nuclear fuel samples as described in previous work [16]. In brief, the

spent nuclear fuel element was cut open in a hot cell facility. A small amount of the spent nuclear fuel was dissolved in concentrated nitric acid. The solution was diluted based on the theoretical amount of Cm expected in the sample using the Monte-Carlo physics code SERPENT (version 2-2.1.31) [23] to reduce the radioactivity for handling during the separation. The solution radioactivity was tested to ensure staff safety before sending the samples from the hot cells to the laboratory. The sample solution was brought to 8 M HNO₃ and passed through sequential UTEVA and DGA resins (Eichrom, Lisle, IL, USA). The UTEVA resin was discarded and Cm was eluted with 20 ml of 0.1 M HCl from the DGA resin.

The Cm solution also contained Am and lanthanide impurities, which were removed as described in previous work [16]. An aliquot of 2 ml for the sample solution was evaporated to dryness. The residue was re-dissolved with 5 ml of 4 M NH₄SCN + 0.1 M formic acid solution. The solution was passed through a TEVA resin. The resin was rinsed with 10 ml of 4 M NH₄SCN + 0.1 M formic acid solution. The actinides were eluted from the resin using 20 ml of 1 M HCl. The absence of radioactive lanthanides (mainly Eu isotopes) was verified by gamma spectrometry. The separation was repeated if needed.

Americium needed to be removed because its amount was too high for being introduced into the AMS. The separation of Am and Cm was done using a method previously developed [24]. The solution containing Am and Cm was evaporated to dryness and re-dissolved with 10 ml of 0.16 M Na₂S₂O₈ + 0.005 M AgNO₃ in 0.01 M HNO₃. The solution was heated to 80 °C to oxidize Am(III) to Am(V). The solution was then passed through a DGA resin, which selectively retained Cm(III) from Am(V). Curium was eluted from the resin using 15 ml of 0.1 M HCl. A small aliquot of the solution was used to verify the absence of Am by alpha spectrometry (~0.05 ml). The alpha thin-layer source was prepared using a CeF₃ micro-precipitation as described in reference [25]. The separation was repeated if needed until no Am was detected.

AMS target preparation

Solutions containing 0.1 mg of Fe(III) and 0.4 mg of Ti(IV) were added to 2 ml of the purified Cm solution. The pH was raised to pH 9 using ammonium hydroxide. The precipitate was centrifuged and the supernatant was discarded. The precipitate was transferred into a quartz crucible using methanol. The methanol was evaporated and the residue was heated to 600 °C for approximately 4 h and then cooled down. The sample was mixed with 5 mg of Nb powder directly in the quartz crucible using a disposable pestle. The mixed sample was pressed onto an aluminum ball in an AMS sample holder.

No recovery tracer was added to prevent contamination of the sample with ²⁴⁴Cm, ²⁴⁵Cm, and ²⁴⁶Cm. Therefore, the method chemical recovery was not determined. The chemical recovery was sufficiently high to be able to measure the Cm isotopes needed for this work with an acceptable precision.

Model age calculation

Calculations of the model age and related uncertainties have been done as described in previous work [16]. In short, net counting rates were calculated for each isotope by subtracting the blank counting rate from the measured counting rate. The net counting rates were corrected for radioactive decay using the known time elapsed since the end of irradiation of the fuel samples. Finally, the isotopic ratios of ²⁴⁴Cm/²⁴⁶Cm and ²⁴⁵Cm/²⁴⁶Cm at the end of irradiation were calculated from the decay corrected net counting rates. Gaussian error propagation was used to determine the uncertainties of the isotopic ratios, taking into account the uncertainties of both the measured counting rates and the average method blanks counting rate. The time elapsed since the end of irradiation including its uncertainty was calculated as described in our initial publication [16] using Eqs. (7) and (8).

Results and discussion

Cm ratios measured

The measured Cm count rates of the spent nuclear fuel samples presented in this study are shown in Table 2. These data were used to calculate the measured and decay-corrected at end of irradiation ²⁴⁴Cm/²⁴⁶Cm and ²⁴⁵Cm/²⁴⁶Cm ratios, which are presented in Table 3.

The 16 samples from the initial study [16] were re-analyzed together with two newly prepared AMS targets of sample E-4 of this study as external standard to obtain

Table 3 Measured (R_1) and decay-corrected (R_0) Cm isotopic ratios

Fuel ID	Measured molar ratios (R_1)		Decay-corrected molar ratios at end of irradiation (R_0)	
	²⁴⁴ Cm/ ²⁴⁶ Cm ± 1σ	²⁴⁵ Cm/ ²⁴⁶ Cm ± 1σ	²⁴⁴ Cm/ ²⁴⁶ Cm ± 1σ	²⁴⁵ Cm/ ²⁴⁶ Cm ± 1σ
E-1	324 ± 8	8.8 ± 0.2	1020 ± 30	8.8 ± 0.2
E-2	590 ± 10	8.6 ± 0.2	1020 ± 20	8.6 ± 0.2
E-3	450 ± 30	7.7 ± 0.5	760 ± 50	7.7 ± 0.5
E-4	740 ± 20	9.1 ± 0.2	1000 ± 20	9.1 ± 0.2
E-5	460 ± 20	6.7 ± 0.3	630 ± 30	6.7 ± 0.3
E-6	660 ± 50	9.5 ± 0.7	1030 ± 70	9.5 ± 0.7

comparable results. In the re-analysis, the average measured and decay-corrected $^{244}\text{Cm}/^{246}\text{Cm}$ and $^{245}\text{Cm}/^{246}\text{Cm}$ molar ratios of sample E-4 were 890 ± 30 and 10.6 ± 0.4 , respectively, which are 16% and 21% higher than the results for sample E-4 presented here. As a consequence, all $^{244}\text{Cm}/^{246}\text{Cm}$ and $^{245}\text{Cm}/^{246}\text{Cm}$ ratios of the initial study were divided by 1.16 and 1.21, respectively. The results of the normalized and decay-corrected isotopic ratios of the re-analysis study are listed in the Appendix (Tables 5 and 6).

Curium ratios relation

The $^{244}\text{Cm}/^{246}\text{Cm}$ ratios as a function of the $^{245}\text{Cm}/^{246}\text{Cm}$ ratios are shown in Fig. 1 for the re-analyzed initial study samples (normalized data) and the current study samples. The data from the initial study [16] are shown for comparison.

A refined reference curve for the Cm chronometry model was created by linearizing the data set and applying a linear fit that takes into account errors in the x and y directions [26]. The fit parameters of the underlying power law $y = c x^b$ were determined to be $c = 48.63 \pm 1.87$ and $b = 1.359 \pm 0.024$. A reduced Chi-squared value of 2.27 was calculated when comparing the measured data with the fit and taking into account the analytical uncertainties of the data points. This value was larger than the upper limit of 1.73 given by 19 degrees of freedom and 95% confidence limit, indicating that the scatter of the data was larger than the analytical uncertainties. By quadratically adding an external uncertainty to each data point the external scatter could be determined.

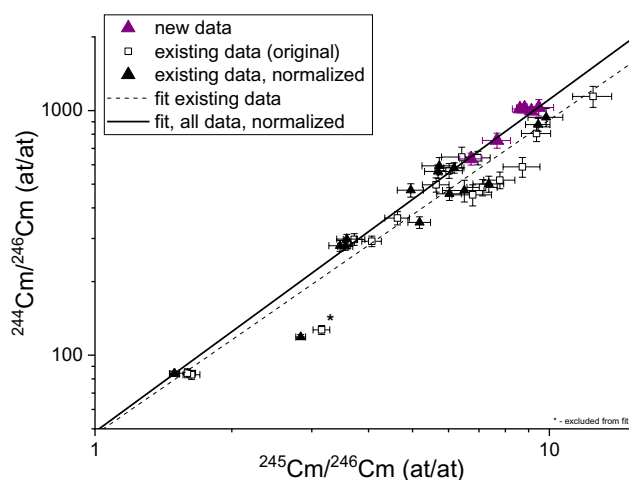


Fig. 1 $^{244}\text{Cm}/^{246}\text{Cm}$ as a function of $^{245}\text{Cm}/^{246}\text{Cm}$ ratio for the new data (filled purple triangles), normalized initial data (filled black triangles), and the initial data (open squares) for comparison. The updated reference curve (straight line) considers only the new data and the normalized data from the initial study (filled purple and black triangles). The linear fit to the initial study data is shown for comparison (dashed line)

By adding an external uncertainty of 2.6% to the data set, a reduced Chi-squared value of 1.73 was obtained. Consequently, for the calculation of the fit parameters and their uncertainties an external uncertainty of 2.6% was quadratically added to each data point.

Combining the current study data together with the normalized data from the initial study led to a more precise reference curve for the Cm chronometry model. The uncertainties of the fit parameters c and b were reduced from 6.3% and 3.2% (initial study) to 3.8% and 1.7% (this study), respectively, which should translate into more precise ages for unknown spent nuclear fuel samples. Indeed, when treating all samples as unknowns, the uncertainty of the calculated ages is reduced from 3.9 yr (initial study reference curve) to 2.7 yr with the new reference curve. In addition, the current data (E series) align relatively well with the initial data using completely different fuels, which supports the validity of the Cm age-dating radiochronometry model.

Spent nuclear fuel ages.

The calculated and actual spent nuclear fuel ages since last irradiation are shown in Table 4 and plotted in Fig. 2. The data from the initial study [16] are reported in Table 4 and Fig. 2 and decay-corrected for comparison. Also, the differences between the actual and calculated discharge ages from both studies are shown in Table 4. Note that the fuel discharge age uncertainty is sometimes significantly higher than the measurement uncertainty because the fuel age uncertainty depends on the accuracy of the reference curve.

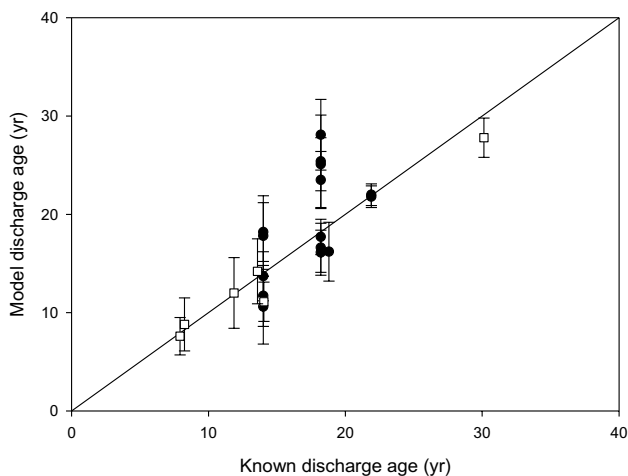
The mean absolute differences between the calculated and actual discharge ages of the fuel for the samples from the initial study (fuels A to D) remained essentially the same (3.4 ± 2.2 yr and 3.3 ± 2.8 yr, respectively) (Table 4). Therefore, adding data for new fuels to the curve (E series) did not improve the accuracy of the initial study data (fuels A to D). When considering only the new fuels that had continuous irradiation (E series), the mean absolute difference with the expected ages of 1.2 ± 1.2 yr was significantly lower. The accuracy of the calculated ages was substantially improved for these data only. This could be because the fuel had continuous irradiation, but more data would be needed to confirm this hypothesis due to the limited amount of data available ($n=6$). Finally, the mean absolute age difference of all the normalized data was 2.7 ± 2.6 yr, which is slightly better than the 3.4 ± 2.2 yr of the initial study. The overall mean relative average was lower solely because of the addition of the new fuel data (E series).

The reference curve cannot be prepared using only the current study data because the new data span over only a

Table 4 Calculated fuel age after irradiation

Fuel ID	Fuel actual age* (yr)	Calculated age* (yr)		Age difference (yr)		Variation between studies (yr)
		Initial	Current	Initial	Current	
A-1	14.0	8.2±4.9	10.6±3.8	5.8	3.5	2.4
A-2	14.0	9.4±3.9	11.7±3.1	4.6	2.3	2.3
A-3	14.0	11.1±3.8	13.7±2.5	2.9	0.3	2.6
A-4	14.0	15.6±5.3	17.8±4.1	-1.6	-3.8	-2.2
A-5	14.0	15.1±4.3	18.2±3.0	-1.1	-4.2	-3.1
B-1	18.2	17.8±3.1	17.7±1.8	0.4	0.5	-0.1
B-2	18.2	14.3±3.2	16.1±2.3	3.9	2.1	1.8
B-3	18.2	16.4±3.5	16.6±2.5	1.8	1.7	0.1
B-4	18.2	23.6±5.0	25.4±4.7	-5.3	-7.1	-1.8
B-5	18.2	23.4±4.2	23.5±2.9	-5.2	-5.2	-0.1
B-6	18.2	24.6±4.3	25.1±2.7	-6.3	-6.9	-0.6
B-7	18.2	25.1±4.9	28.1±3.6	-6.9	-9.9	-3.0
C-1	21.9	23.6±2.5	22.0±1.1	-1.7	-0.1	1.6
C-2	21.9	22.5±2.5	21.8±1.1	-0.6	0.0	0.5
D-1 ^b	21.2	34.0±2.7	34.9±1.3	-12.8	-13.7	2.4
D-2	18.8	15.4±3.8	16.2±3.0	3.4	2.6	2.3
E-1	30.13	–	27.8±2.0	–	2.3	–
E-2	14.04	–	11.1±2.0	–	2.9	–
E-3	13.58	–	14.2±3.3	–	-0.7	–
E-4	7.92	–	7.6±1.9	–	0.3	–
E-5	8.25	–	8.8±2.7	–	-0.6	–
E-6	11.86	–	12.0±3.6	–	-0.1	–
Mean absolute difference (all data)					2.7±2.6	
Mean absolute difference (initial data only)				3.4±2.2	3.3±2.8	1.6±1.1
Mean absolute difference (current data only)					1.2±1.2	

*Relative to the measurement date

^bThe outlier point is not included in the mean absolute difference calculation**Fig.2** Model discharge age as a function of the known age (full circle: initial study, empty squares: this study)

small range on the $^{245}\text{Cm}/^{246}\text{Cm}$ axis (Fig. 1). The extrapolation of the fit into regions far beyond this range would substantially increase the uncertainty of the calculated ages. Fuels with a wider range of burnups, i.e., lower and higher than the burnup values of the current study, would be needed to improve the reference curve.

Performance of the Cm radiochronometer

The $^{241}\text{Am}/^{241}\text{Pu}$, $^{242}\text{Pu}/^{240}\text{Pu}$ vs $^{241}\text{Pu}/^{239}\text{Pu}$ and $^{90}\text{Sr}/^{88}\text{Sr}$ radiochronometers can predict the model discharge age of nuclear spent fuels with an accuracy of a few years (e.g. $\pm 1\text{--}6$ yr) [12–14]. This is comparable with the Cm radiochronometry age model developed. Radiochronometers developed to determine model ages of purified U and Pu materials have a much higher accuracy of up to 1 month [7], mainly because the parent radionuclide and its progeny

have been separated at $t=0$, which is not the case with spent nuclear fuel. If the Cm radiochronometry method developed is applied to reprocessed fuels, consideration needs to be made of the possible contribution of Cm isotopes from the first irradiation, and thus the model discharge date would be a composite of the two irradiations.

A potential solution to increase the accuracy of the Cm radiochronometer could be to have correction factors derived from other isotopes to account for the discontinuous irradiation in the reactor. It has been suggested [27] that ^{147}Sm could be used to estimate how long the reactor was shut down, but this has never been experimentally demonstrated. Note that ^{147}Sm has not been measured for this project and cannot be verified with the current data.

All measurements have been normalized using sample E-4, which makes it more challenging for interlaboratory comparison. The development of a reference material would enable other laboratories to make comparable measurements and provide a way to correct for laboratory, process, and instrument specific bias between laboratories. The Cm isotopic composition of the reference material could be established using mass spectrometric methods such as inductively coupled mass spectrometry (ICP-MS), thermal ionization mass spectrometry (TIMS), and AMS.

Conclusions

A three Cm isotopes system was refined to determine the model discharge ages of spent nuclear fuels. This radiochronometer is applicable for spent fuel not purified at time of discharge. A discontinuous irradiation of the nuclear fuel was presumed to be a limitation of the Cm chronometry reference curve due to the significant decay of ^{244}Cm when the irradiation is stopped. Six fuel samples that were continuously irradiated were used to verify this assumption. Adding these new data improved the precision of the $^{244}\text{Cm}/^{246}\text{Cm}$ as a function of $^{245}\text{Cm}/^{246}\text{Cm}$ fit curve. It also slightly improved the accuracy of the fuel age determination from 3.3 ± 2.8 to 2.7 ± 2.6 yr, respectively, on average. The model ages

determined with the added fuel samples from the current study, 1.2 ± 1.2 yr, were on average more accurate than the initial study. The results of this study suggest that a discontinuous irradiation of the fuel adds to the uncertainty of the determined age. Further improvements of the reference curve would require a much larger number of data. Comparison of this radiochronometer to others would be interesting, including for the case of reprocessed fuel.

Appendix

See Tables 5 and 6.

Table 5 Re-analysis of samples from the initial study: average counting rates measured by AMS for ^{244}Cm , ^{245}Cm , and ^{246}Cm in samples and blanks

Fuel ID	Blank corrected counting rate (cps)		
	$^{244}\text{Cm} \pm 1\sigma$	$^{245}\text{Cm} \pm 1\sigma$	$^{246}\text{Cm} \pm 1\sigma$
A-1	239 ± 1	3.79 ± 0.08	0.57 ± 0.04
A-2	314 ± 2	5.2 ± 0.1	0.79 ± 0.05
A-3	479 ± 2	8.4 ± 0.1	1.16 ± 0.05
A-4	349 ± 2	6.0 ± 0.1	0.53 ± 0.04
A-5	520 ± 3	9.2 ± 0.1	0.84 ± 0.05
B-1	359 ± 2	8.9 ± 0.1	2.14 ± 0.06
B-2	230 ± 1	5.3 ± 0.1	1.28 ± 0.05
B-3	181 ± 1	4.33 ± 0.09	1.07 ± 0.05
B-4	121.5 ± 0.6	3.24 ± 0.08	0.43 ± 0.04
B-5	234 ± 1	6.0 ± 0.1	0.85 ± 0.05
B-6	205 ± 1	5.9 ± 0.1	0.97 ± 0.05
B-7	187.0 ± 0.9	5.3 ± 0.1	0.62 ± 0.04
C-1	2260 ± 10	89.7 ± 0.5	51.3 ± 0.3
C-2	1452 ± 7	57.4 ± 0.3	32.9 ± 0.2
D-1	1261 ± 6	65.3 ± 0.4	19.7 ± 0.1
D-2	220 ± 1	4.57 ± 0.09	0.79 ± 0.05
	Counting rate (cps)		
Blanks ($n=3$)	0.4 ± 0.1	0.013 ± 0.006	0.02 ± 0.04

Table 6 Cm isotopic ratios calculated from the re-analysis of samples from the initial study: measured isotopic ratios (R_1), isotopic ratios normalized to the external standard E-4 (R_{1_E-4}), and normalized and decay-corrected isotopic ratios (R_{0_E-4})

Fuel ID	Measured isotopic molar ratios (R_1)		Normalized molar ratios (R_{1_E-4})		Decay-corrected and normalized molar ratios (R_{0_E-4}) at end of irradiation	
	$^{244}\text{Cm}/^{246}\text{Cm}$ $\pm 1\sigma$	$^{245}\text{Cm}/^{246}\text{Cm}$ $\pm 1\sigma$	$^{244}\text{Cm}/^{246}\text{Cm}$ $\pm 1\sigma$	$^{245}\text{Cm}/^{246}\text{Cm}$ $\pm 1\sigma$	$^{244}\text{Cm}/^{246}\text{Cm}$ $\pm 1\sigma$	$^{245}\text{Cm}/^{246}\text{Cm}$ $\pm 1\sigma$
A-1	420±30	6.7±0.5	350±30	5.7±0.5	590±50	5.7±0.5
A-2	400±20	6.6±0.4	330±20	5.7±0.4	560±30	5.7±0.4
A-3	410±20	7.2±0.3	340±20	6.2±0.4	580±30	6.2±0.3
A-4	660±60	12±1	550±50	9.9±0.8	940±80	9.8±0.8
A-5	620±30	11.0±0.6	510±30	9.5±0.5	880±50	9.5±0.5
B-1	168±5	4.2±0.1	139±4	3.6±0.1	278±8	3.6±0.1
B-2	180±7	4.2±0.2	149±6	3.6±0.2	300±10	3.6±0.2
B-3	169±8	4.0±0.2	140±6	3.5±0.2	280±10	3.5±0.2
B-4	280±30	7.6±0.8	240±20	6.5±0.7	470±50	6.5±0.7
B-5	280±20	7.0±0.4	230±10	6.0±0.4	460±30	6.0±0.4
B-6	210±10	6.0±0.3	174±9	5.2±0.3	350±20	5.2±0.3
B-7	300±20	8.6±0.6	250±20	7.4±0.6	500±40	7.4±0.6
C-1	44.0±0.3	1.75±0.01	36.4±0.3	1.50±0.01	83.8±0.6	1.50±0.01
C-2	44.0±0.3	1.74±0.01	36.5±0.3	1.50±0.01	84.0±0.6	1.49±0.01
D-1*	63.9±0.6	3.31±0.03	52.9±0.5	2.84±0.03	119±1	2.84±0.03
D-2	280±20	5.8±0.4	230±10	5.0±0.3	470±30	5.0±0.3

*Not used in the reference curve

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Declarations

Conflict of interest The authors have no relevant financial nor non-financial interests to disclose. The authors have no conflict of interest to disclose. The authors have no competing interests to declare that are relevant to the content of this article.

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