Title page

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Applications of *MP*-1 Anion Exchange Resin and Eichrom *LN* Resin in Berkelium-249 Purification*

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Abstract

Purification of berkelium-249 (^{249}Bk) at Oak Ridge National Laboratory requires a multi-step process with Bk Finishing as the final step. The current process takes 6 or 7 months, including ~3 months spent on Bk Finishing. Recent trials using columns of either *LN* resin or *MP*-1 anion exchange resin adsorbing the tetravalent $^{249}Bk^{4+}$ in 8 *M* HNO_3-0.5 *M* $NaBrO_3$, followed by eluting impurities (e.g. Ce^{4+}, Cf^{3+}) and stripping ^{249}Bk resulted in a new dual column method of selectively separating ^{249}Bk from other trans-curium elements and fission product impurities, which is proposed to replace the current Bk Finishing with higher Bk purification efficiency and shorter processing period. This paper displays the experimental results and describes the dual column method with relevant chemistry issues.

Keywords ^{249}Bk, *MP*-1 resin, *LN* resin, $NaBrO_3$, Dual Column Method

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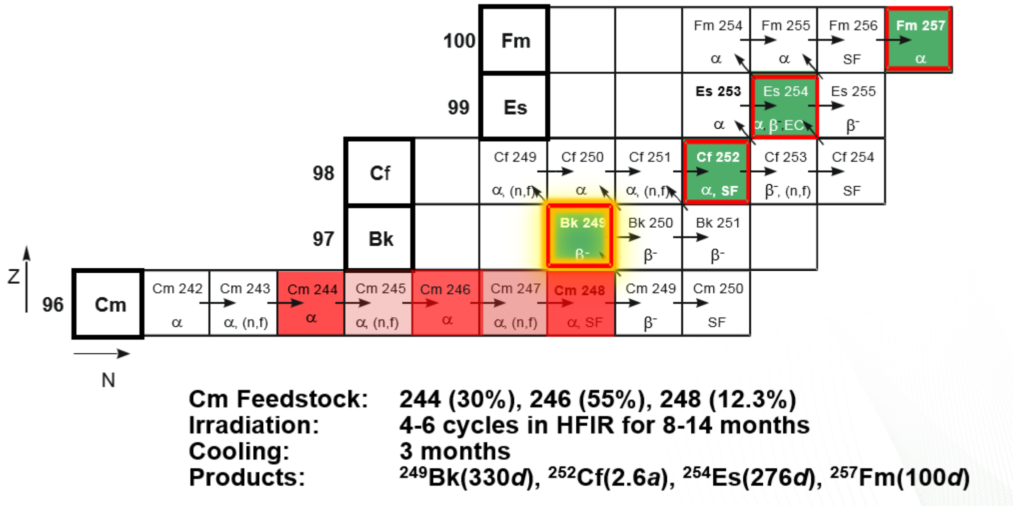
Introduction

The demand for heavy trans-plutonium target materials, including ^{249}Bk (half-life 330 *d*), by the super heavy element (SHE) research community is increasing, but production of these elements requires complex multistep campaigns. ^{249}Bk is produced via successive neutron captures and beta decays of the curium (Cm) feedstock irradiated in the High Flux Isotope Reactor (HFIR) at Oak Ridge National Laboratory (ORNL). **Fig. 1** shows the nuclear reaction route used to produce ^{249}Bk in HFIR, and **Fig. 2** shows the major post-irradiation processing steps after the target discharge and cooling.



Cm Feedstock:	**244 (30%), 246 (55%), 248 (12.3%)**
Irradiation:	**4-6 cycles in HFIR for 8-14 months**
Cooling:	**3 months**
Products:	**^{249}Bk(330*d*), ^{252}Cf(2.6*a*), ^{254}Es(276*d*), ^{257}Fm(100*d*)**

Fig 1 ^{249}Bk produced by neutron captures and beta decays of irradiated Cm feedstock

The CLEANEX step removes most of lanthanide (Ln) FPs from the dissolved irradiated Cm feedstock target. Two LiCl anion exchange (AX) separations further removes Ln FPs from trivalent actinides (An) and separates Cm-Am from trans-Cm isotopes (including ^{249}Bk, ^{252}Cf, ^{254}Es, and ^{257}Fm). The primary separation of ^{249}Bk from other trans-Cm isotopes is accomplished via cation exchange (CX) with α-hydroxyisobutyrate (AHIB) in a hot cell. Bk Finishing, the final purification step for ^{249}Bk product, removes all other residual impurities from ^{249}Bk.

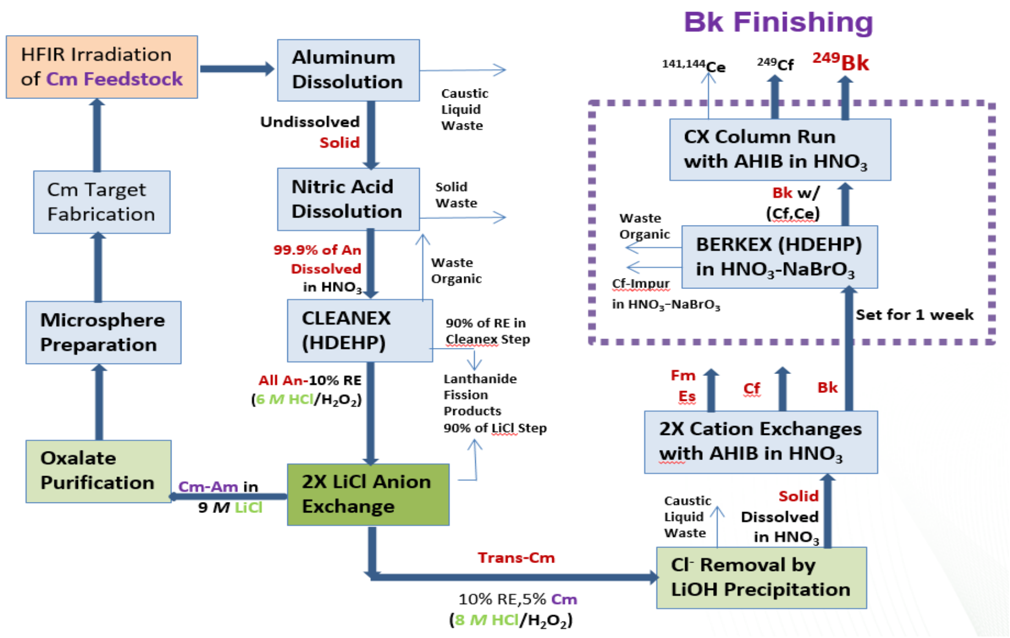


Fig 2 Major steps of the post-irradiation processing of the irradiated Cm feedstock target

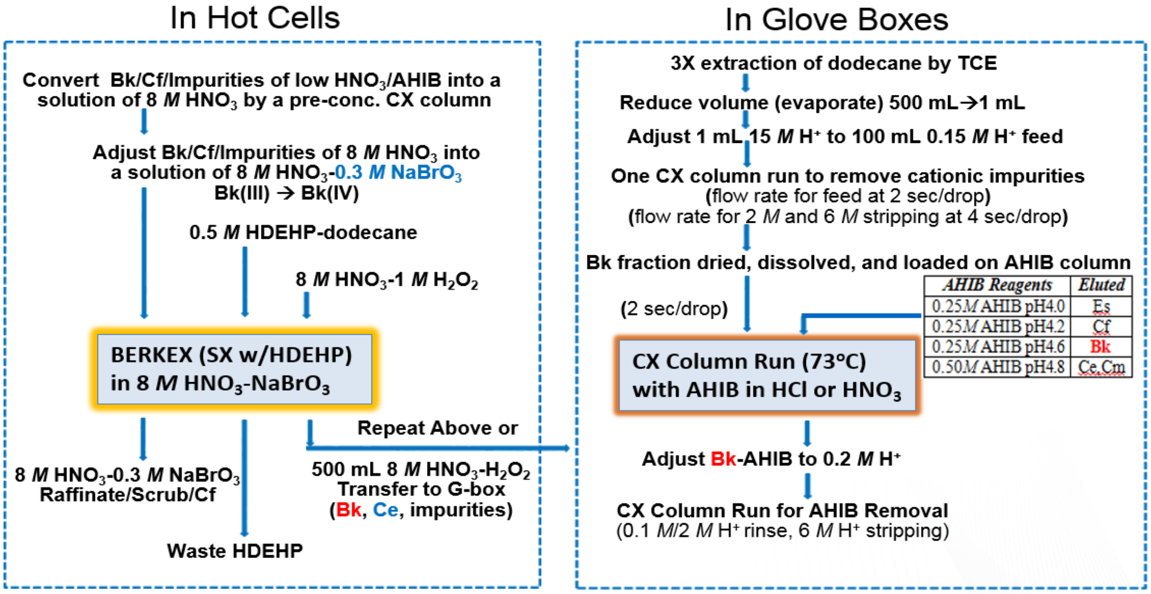
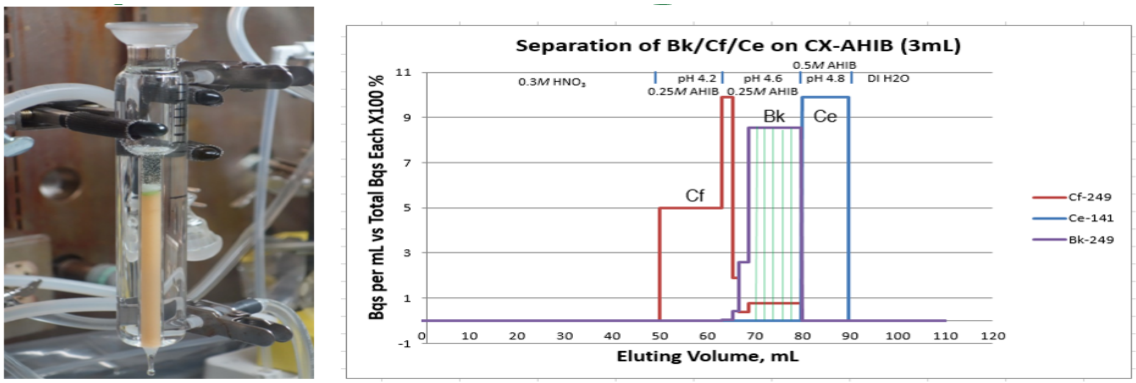


Fig 3 Major operation steps of BERKEX in hot cell and AHIB in a glove box

Bk Finishing includes two major steps, as shown in **Fig. 3**: solvent extraction with HDEHP-dodecane (BERKEX) in 8 M HNO_3–0.3 M $NaBrO_3$ solution in a hot cell and CX column runs with AHIB in a glove box. In the BERKEX process, Bk^{3+} is oxidized to Bk^{4+} by BrO_3^- and extracted by HDEHP in 8 M HNO_3. Ce^{4+} (an oxidized Ln FP) is also extracted by

HDEHP. After two BERKEX runs, a raw Bk fraction in 500 mL of 8 *M* HNO_3-0.45 *M* H_2O_2 is produced and transferred to a glove box for CX AHIB runs.

Glove box AHIB operations include residual organic (dodecane) removal and three cation exchange resin column runs: one for pre-concentrating all cations to prepare the feed for the CX AHIB column run; the second is the AHIB column run itself for final purification of ^{249}Bk; the third is for AHIB removal from the ^{249}Bk product cut of the AHIB run. The AHIB column run employs AHIB as a competing ligand (COO^-) in the mobile phase to compete with the cation exchange resin (SO_3^-)'s ability to adsorb cations. By increasing the strength of AHIB (increasing pH or AHIB concentration), the cations on the column would be eluted in the order of their charge densities (for actinides of same valence, in order of their ion sizes, e.g. Fm^{3+}, Es^{3+}, Cf^{3+}, and then Bk^{3+}). The operation of the AHIB column requires strict control of pH, flow rate, column temperature, and careful cutting of the effluent. Because the Bk and Cf peaks are very close in AHIB column run, a small portion of Cf peak tail may be collected into the ^{249}Bk product cut.



3 mL column: Dowex 50W X8 Resin (73°C)
Adjust berkelium solution to 0.1 *M* HCl
Add ~8 CV 0.3 *M* NH_4NO_3 (convert resin)
Add ~2 CV water to remove nitrates
Add ~4 CV 0.25 *M* pH 4.2 AHIB (Cf)
Add ~5 CV 0.25 *M* pH 4.6 AHIB (Bk)
Add ~3 CV 0.25 *M* pH 4.8 AHIB (Ce)

Feed:
7.22E11 Bq ^{249}**Bk** 13 mg
9.75E7 Bq ^{249}**Cf** 8.5 µg
1.70E7 Bq ^{141}**Ce** 1.6E-4 µg
Components normalized to 1
with **Y axis for % distribution**

^{249}Bk Product:
6.78E11 Bq ^{249}**Bk** (93.9%)
4.04E6 Bq ^{249}**Cf** (4.1%)
No ^{141}**Ce** in shipped product

Fig 4 Details of the glove box operations of AHIB column run in Campaign-77

Fig. 4 provides some detailed information on the glove box AHIB run of Campaign-77 (C-77) conducted in July 2017. The AHIB column elution profile shows the run as a chromatographic elution process with strict control of temperature (73^{o}C), pH (4.2, 4.6, and 4.8), and flow rate (counting seconds/drop) with an argon pressure regulator. The "fraction cut of ^{249}Bk product" (the shaded portion) in the AHIB run of C-77 achieved a 94% recovery of ^{249}Bk from the feed, but with 4.1% of ^{249}Cf carried over from the feed [these percentages are after deduction of the sample ingrowth ^{249}Cf (half-life 351 years) due to ^{249}Bk decay during the 27.5 hours from sample collection to activity analyses].

Note: y- axes of all elution plots in this paper are in Bq/mL vs each isotope's total Bq and expressed in percentage distribution of each isotope (normalized to 1) with the same peak areas of the isotopes along the column elution (x-axis is in mL).

Post-irradiation processing of C-77 took 7 months, including over 3 months of Bk Finishing. To increase ^{249}Bk productivity by shortening the processing, two kinds of resins were tested with a feed from combined fractions of C-77 glove box AHIB run (except for the product fraction with 13 mg of ^{249}Bk): Eichrom® *LN* resins and BioRad® *MP*-1 anion exchange resins.

Experimental

REAGENTS, RESINS, AND RADIONUCLIDES

Nitric acid (69-70% ACS Grade, HNO_3) was purchased from BDH and 2 *M* $NaBrO_3$ was prepared with solid $NaBrO_3$ of 99+% purity purchased from ACROS Organics. The BioRad® *MP*-1 resin with a particle size of 100-200 mesh was purchased from BioRad. The Eichrom® *LN* resin with a particle size of 100-150 μ was purchased from Eichrom Tech, Inc. The radionuclide stock used in the trial column runs was from a combination of all cuts in the C-77 AHIB run (except for the cut of ^{249}Bk product), that was passed through CX resin to remove AHIB. This radionuclide stock solution contained 2.6 x 10^{10} Bq (0.4 mg) of ^{249}Bk, 9.75 x 10^{7} Bq (8.5 μg) of ^{249}Cf, 4.44 x 10^{6} Bq (0.22 μg) of ^{252}Cf, 1.7 x 10^{7} Bq (ca. 1.6 x 10^{-4} μg) of ^{141,144}Ce, and other non-radioactive impurities.

PREPARATION OF FEED AND ELUTING SOLUTIONS

0.5 *M* $NaBrO_3$ in 8 *M* HNO_3 worked as oxidizer for $Bk^{3+} \rightarrow Bk^{4+}$. It was prepared by mixing stock of 2 *M* $NaBrO_3$ with stock of 10.67 *M* HNO_3 in a volume ratio of 1:3, only 20~30 minutes before being used for column runs to minimize the BrO_3^- reduction to Br^- or Br_2 in mixed solutions (color of solutions turns to orange). The stock solution of radionuclides was prepared in 10.67 *M* HNO_3 prior to mixing with 2 *M* $NaBrO_3$. Other HNO_3 solutions were prepared by using 15 *M* HNO_3 diluted with deionized (DI) H_2O to the desired HNO_3 concentrations. 8 *M* HNO_3-0.45 *M* H_2O_2 solution was prepared as stock solution every other day.

COLUMN PREPARATION

Glass columns of same dimensions and same 3.0 mL resin bed volume (BV), as those of AHIB column, were chosen for the *MP*-1 and the *LN* column runs. Both the *MP*-1 resin and Eichrom *LN* resin were pre-wetted in DI H_2O and packed in two glass columns with internal diameters (ID) of 0.6 cm up to the 3 mL BV mark (the first *LN* column was accidentally assembled up to the 3.3 mL mark). The resin bed heights of the columns (3.0 mL) were 10.5 cm so that the same length-to-diameter (L/D) ratio of 17.5 was used for both columns in the experiments. Prior to and after resin loading, quartz wool was put into the tip of the columns to avoid resin leaking and also placed on top of the resin beds to prevent the resin from mixing. The columns were assembled and pre-conditioned with enough 8 *M* HNO_3 outside the glove box and then conditioned with $\geq$ 3 BV of 8 *M* HNO_3-0.5 *M* $NaBrO_3$ inside the glove box right before feed loading onto the column. All column runs were conducted at room temperature and gravity flow rate, with no external pressure exerted for flow rate control.

OPERATIONS OF COLUMN RUNS

Each 8 *M*-HNO_3-conditioned resin column, after bagging into a glove box, needs to be conditioned with $\geq$ 3 BV of 8 *M* HNO_3-0.5 *M* $NaBrO_3$ solution prior to use. The feed solution for each column run was prepared by adding 2 *M* $NaBrO_3$ to the aliquots of the stock radionuclide of 10.67 *M* HNO_3 in a volume ratio of 1:3 and mixed by shaking. The feed solution was allowed to stand for 20~30 minutes to ensure complete oxidation of ^{249}Bk.

The *LN* resin column (3.3 mL) run and *MP*-1 resin column (3.0 mL) run, each used half of the above-mentioned stock solution of radionuclides as feed solution. A second *LN* resin column (3.0 mL) run used the combined fractions from the first *LN* column run as the feed. After loading the feed, three or more washes (8 *M* HNO_3-0.5 *M* $NaBrO_3$) of the vial of radionuclide stock were added to the column. Then, the eluting solution of 8 *M* HNO_3-0.5 *M* $NaBrO_3$ was added to the column. This portion of feed + washes + elution with 8 *M* HNO_3-0.5 *M* $NaBrO_3$ was presumed to be a collection of radionuclides without the ^{249}Bk product.

In the first *LN* run, the portion of 8 *M* HNO_3-0.5 *M* $NaBrO_3$ was 9.2 BV including 1.7 BV of feed/washes. In *MP*-1 run, the portion of 8 *M* HNO_3-0.5 *M* $NaBrO_3$ was 10 BV including 2.3 BV of feed/washes. In the second *LN* run, the portion of 8 *M* HNO_3-0.5 *M* $NaBrO_3$ was 11 BV including 6.8 BV of feed/washes. After column elution with 8 *M* HNO_3-0.5 *M* $NaBrO_3$, various solutions were used for stripping ^{249}Bk off or selectively eluting $^{141.144}$Ce off the column.

SAMPLE ANALYSES

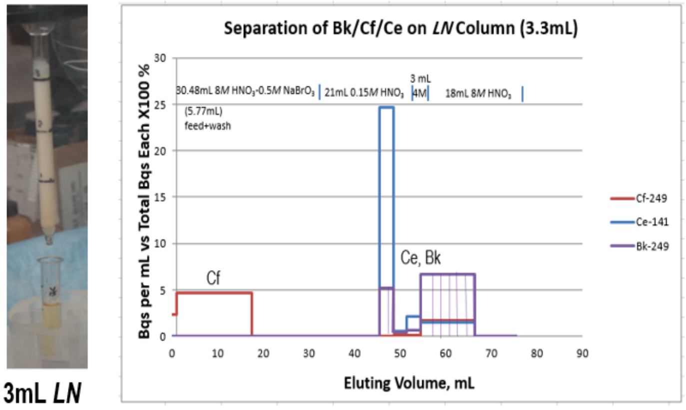
The Analytical Group at the Radiochemical Engineering Development Center (REDC) of ORNL is well equipped with a variety of radiological analyses instrumentation, including HPGe gamma spectrometers, alpha spectrometers (PIPS Detectors), ICP-MS (Thermo Fisher iCAP Q). Due to the REDC's liquid scintillation counter being temporarily unavailable, samples for ^{249}Bk were measured using a gas-flow proportional counter based on calibrations made with a ^{249}Bk sample pre-measured by a Perkin Elmer 5110TR liquid scintillation counter. Samples of ^{249}Cf were measured by both gross alpha and gamma spectrometric methods, based on alpha energies of 5.78 MeV (0.26%) and 5.81 MeV (82.2%), and gamma energies of 333.5 keV and 388.3 keV. Samples for ^{141,144}Ce were measured using a gamma spectrometric method, based on their typical gamma energies 145.4 keV (141Ce) and 133.5 keV (144Ce). Some of the samples of ^{249}Cf and ^{141,144}Ce were measured using a GMX-25 Coaxial HPGe gamma spectrometer, based on typical gamma energies in a relatively high background lab environment.

Results and discussion

LN RESIN COLUMN RUN

Eichrom® *LN* resins consist of porous polymer (Amberchrom® CG71) particles of selected dimensions impregnated with Di-(2-ethylhexyl) phosphoric acid (HDEHP). The chemistry of *LN* resin column run with feed/wash in 8 *M* HNO_3-$NaBrO_3$ is the same in principle **[1]** as that of the BERKEX process, the only difference being the extractant as one was in solid resin form and the other in liquid organic form. The change from a one-stage-solvent extraction (SX) process to a column separation has the advantages of a high number of theoretical stages for ^{249}Bk adsorption onto *LN* resins, and no organic liquid waste (HDEHP) disposal issues; however, operating parameters, such as the amount of ^{249}Bk vs resin bed size, proper L/D of the resin bed, and volumes of each fraction cut need to be determined in trial runs.

Knowing both Bk (IV) and Ce (IV) were being adsorbed on *LN* resin (HDEHP), an attempt was made to selectively elute ^{141,144}Ce ahead of ^{249}Bk off the column by eluting the *LN* resin column with 0.15 *M* HNO_3 after Cf removal by 8 *M* HNO_3-0.5 *M* $NaBrO_3$, followed with ^{249}Bk stripping with other reagents.



3 mL *LN* column:

Feed in 8 *M* HNO_3-0.5 *M* $NaBrO_3$
Elution with 8 *M* HNO_3-0.5 *M* $NaBrO_3$
Trial eluting Ce with 0.15 *M* HNO_3 only
Trial eluting Ce with 4 *M* HNO_3
Stripping with 8 *M* HNO_3 No H_2O_2

Results:

Complete separation of Cf (not retained), going with 8 *M* HNO_3-0.5 *M* $NaBrO_3$
Bk and Ce retain, follow-up separation of Ce from Bk unsuccessful

Fig 5 The elution profile of *LN* (3.3 mL) resin column run

The *LN* column elution profile is shown in the **Fig. 5**. The *LN* resin column (3 mL) run was performed in the following elution order: 9.2 BV of 8 *M* HNO_3-0.5 *M* $NaBrO_3$ including 1.7 BV (5.77 mL) of feed/washes, 6.4 BV of 0.15 *M* HNO_3, 1 BV of 4 *M* HNO_3 and 6.4

BV of 8 *M* HNO_3. Co-adsorption of Bk and Ce with complete removal of Cf was as expected. Complete removal of Cf (III) and other impurities of divalent/trivalent can be achieved within 6 BV of 8 *M* HNO_3-0.5 *M* $NaBrO_3$ including 1.7 BV of feed loading fraction, with both Bk and Ce firmly retained on resins after more than 10 BV of 8 *M* HNO_3-0.5 *M* $NaBrO_3$ elution, making the *LN* column work as a "cut-off" column with no requirements of chromatographic control of effluent volume.

To confirm a complete removal of Cf (III) on *LN* column in the event of a much larger volume of feed loading, an additional *LN* column run was performed in the elution order of 12 BV of 8 *M* HNO_3-0.5 *M* $NaBrO_3$ including 6.8 BV (20.3mL) of feed/washes, 2 BV of 0.15 *M* HNO_3, 2.1 BV of 4 *M* HNO_3 and 4 BV of 8 *M* HNO_3-0.45 *M* H_2O_2 (**Fig. 6**).

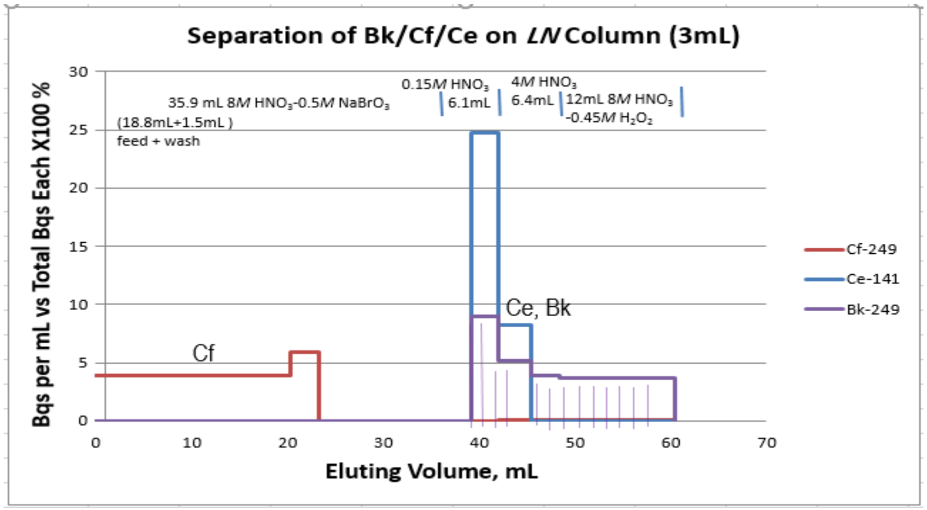


Fig 6 The elution profile of second *LN* resin column (3 mL) run

A larger volume of feed solution may occur when directly using the Bk stripping fraction from an early column run after addition of $NaBrO_3$ but without volume reduction, in order to shorten the campaign process. The second *LN* column run with a 6.8 BV of feed/wash solution resulted in a complete Cf removal within 8 BV of 8 *M* HNO_3-0.5 *M* $NaBrO_3$ elution, even though the total elution of 8 *M* HNO_3-0.5 *M* $NaBrO_3$ was in 11 BV.

Two *LN* column runs proved the complete removal of Cf and divalent/trivalent impurities from Bk (IV) and Ce (IV) which were adsorbed onto the *LN* resins. Further elution with 0.15 *M* HNO_3 was performed based on a study by Moore **[2]** for the purpose of selectively eluting $^{141,144}Ce$ off the column ahead of the ^{249}Bk stripping. Obviously, the selective stripping $^{141,144}Ce$ by 0.15 *M* HNO_3 was unsuccessful, with overlapping peaks of Ce and Bk in both *LN* column runs. In case of the first run, if the effluent cut at the high Ce peak (45.5 to 48.5 mL), only 70.7% of the total Ce would be removed but with a loss of 13.1% of ^{249}Bk product. If the cut were expanded (45.5 to 51.5 mL), 78.5% of the total Ce would be removed but with a loss of 15.8% of ^{249}Bk product, which is certainly not favorable to ^{249}Bk production.

In Moore et al. report, a *LN* resin column (1.4 mL of L/D = 14) was used to separate trace amounts of ^{249}Bk and ^{144}Ce, where ^{144}Ce was completely removed with 7 BV of 0.15 *M* HNO_3 elution without overlap and with a follow up ^{249}Bk peak. By comparing Moore's experimental conditions to ours, Moore et al. were successful due to three main reasons:

(1) Moore used only tracer amounts of ^{144}Ce and ^{249}Bk, respectively 7 thousand and 4 million times lower amounts than in this work. Much narrow peak widths for both ^{144}Ce and ^{249}Bk minimized the chance of the peak overlapping;

(2) Moore used a feed of trivalent Bk (III) and Ce (III), while the selective eluting of this work with 0.15 *M* HNO_3 starts with a transit process for Bk (IV) and Ce (IV) to be reduced to trivalent states, which complicated their elution order;

(3) The most important reason may be that Moore's feed volume was always controlled at 14% of the BV, while our 0.15 *M* HNO_3 elution started after more than 10 BV of 8 *M* HNO_3-0.5 *M* $NaBrO_3$ elution in which both ^{144}Ce and ^{249}Bk had already migrated down into the column; therefore, the case of second *LN* resin column run with 12 BV of 8 *M* HNO_3-0.5 *M* $NaBrO_3$ was even worse, in term of Ce/Bk separation, than the first *LN* resin column run with 10 BV of 8*M* HNO_3-0.5*M* $NaBrO_3$.

Other journal studies found that 0.15*M* HNO_3 may not be the optimal acidity for $^{141,144}Ce$ to be selectively eluted off column ahead of ^{249}Bk. An ORNL report by Knauer **[3]** indicates that the affinity of both ^{249}Bk and ^{144}Ce to HDEHP increases as the concentration of the eluting HNO_3 decreases, but with a big difference. For example, at 1.0 *M* HNO_3, the K_d of Bk is 3 while that of Ce is only 0.03; at 0.15 *M* HNO_3, the K_d of Bk is 100 while that of Ce is unknown but with a tendency towards a value higher than 1. Hence elution using HNO_3 concentrations of >0.15 *M* but <1.0 *M* on a *LN* column may be the next candidate for separating Bk and Ce after the Cf removal.

The open literature and our own experience show that H_2O_2 in an eluting HNO_3 plays an important role in achieving a quick reduction of tetravalent Bk (IV) and Ce (IV) back to trivalent Bk (III) and Ce (III); otherwise, both Bk (IV) and Ce (IV) are reasonably stable in solution in the absence of reducing agents because of the stabilizing influence of either their half-filled $5f^7$ or empty $4f^0$ subshell respectively.

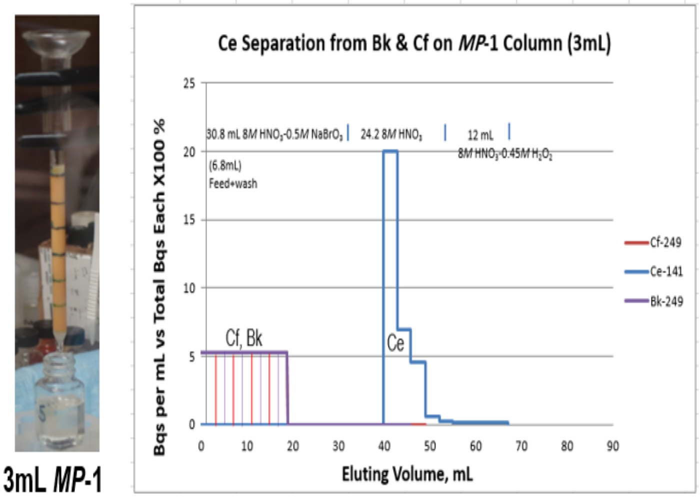
MP-1 RESIN COLUMN RUN

BioRad® *MP*-1 resin has been broadly used in radionuclide separations, especially in actinide separations. Cations in aqueous solution are considered as hydrated ions (ions surrounded with H_2O molecules due to the dipolar force of H_2O molecules and the charge density of ions). For cations (M^{n+}) in high concentrations of an acid solution (HA), H_2O molecules of the inner-sphere of the cation hydrate ions may be replaced by anions (A^-) of the HA, and thus form metal anions (e.g. $MA_m^{(m-n)-}$).

Actinides, particularly those with higher oxidation states, from Th to Bk, may form actinide anions in high concentrations of HCl or HNO_3 and then be adsorbed on AX resins. The most familiar examples include Th (IV) in high HNO_3 (but not in HCl), U (VI) in high HCl (but not in HNO_3) and Pu (IV) in either high HNO_3 or high HCl **[4]**. Bk (IV) has a smaller ionic size than the above mentioned tetravalent actinides (means higher charge density), so the question is will Bk (IV) form anions to be adsorbed onto AX resins.

An *MP*-1 resin column (3.0 mL) run was performed in the following elution order: 10 BV of 8 *M* HNO_3-0.5 *M* $NaBrO_3$ including 2.3 BV of feed/washes, 8 BV of 8 *M* HNO_3 and 4 BV of 8 *M* HNO_3-0.45 *M* H_2O_2. **Fig. 7** shows its elution profile and clearly indicates that the nitrate complexed Ce (IV) anions are adsorbed on *MP*-1 anion exchange resins, while the oxidized Bk (IV) is not adsorbed and is instead eluted out of the column together with trivalent Cf (III).

A complete separation of Ce (retained) from Bk and Cf was achieved within 6.3 BV of 8 *M* HNO_3-0.5 *M* $NaBrO_3$ elution, although 10.3 BV of 8 *M* HNO_3-0.5 *M* $NaBrO_3$ elution was performed in this column run. Since the first 6.3 BV of effluent was collected into same vial, not knowing if the actual Bk/Cf peak ended prior to reaching 6.3 BV of 8 *M* HNO_3-0.5 *M* $NaBrO_3$ elution or not. Even so, the Bk/Cf peak ended with 7 BV apart from the stripped Ce peak.



3 mL *MP*-1 column:

Feed in 8 *M* HNO_3-0.5 *M* $NaBrO_3$
Elution with 8 *M* HNO_3-0.5 *M* $NaBrO_3$
Trial stripping with 8 *M* HNO_3 only
Stripping with 8 *M* HNO_3-0.45 *M* H_2O_2

Results:

Complete separation of Ce (retained)
Bk and Cf not retained, together go with 8 *M* HNO_3-0.5 *M* $NaBrO_3$

Fig 7 The elution profile of *MP*-1 resin column (3 mL) run

In this run, 8 *M* HNO_3 with no addition of H_2O_2 was tested for stripping the adsorbed Ce (IV) off the column, prior to a final stripping with 8 *M* HNO_3-0.45 *M* H_2O_2. It took 6 BV of 8 *M* HNO_3 to strip the majority of the Ce off the column, which proves the necessity of using HNO_3-H_2O_2 to quickly strip Ce in future runs.

The most notable result for this *MP*-1 column run was that the oxidized Bk^{4+} was not adsorbed by the AX *MP*-1 resin. The fact that ^{249}Bk has been oxidized to tetravalent state in this *MP*-1 column run was confirmed because Ce (III) of similar E^o (see **Table-1**) had been oxidized and adsorbed on *MP*-1 resin. Also, in same 8 *M* HNO_3-0.5 *M* $NaBrO_3$ solution of all previous experiments both Bk (III) and Ce (III) were oxidized to tetravalent states and adsorbed on *LN* resins or extracted into the organic extractant HDEHP. Obviously, the only explanation, as to why Bk^{4+} was not adsorbed by *MP*-1 resin similar to Ce^{4+}, would be that the oxidized Bk (IV) did not form anion complexes in 8 *M* HNO_3, and thus was not adsorbed by AX *MP*-1 resin.

Table-1 Standard reduction potentials (E^o) of concerned ions

Half-Reactions	***E^o (V)***
$O_{2\,(g)} + 2\,H^+_{(aq)} + 2e^- \rightleftharpoons H_2O_{2\,(aq)}$	+0.68
$Br_{2\,(l)} + 2e^- \rightleftharpoons 2\,Br^-_{(aq)}$	+1.07
$Cr_2O_7^{2-}{}_{(aq)} + 14\,H^+_{(aq)} + 6e^- \rightleftharpoons 2\,Cr^{3+}_{(aq)} + 7\,H_2O$	+1.33
$Cl_{2\,(l)} + 2e^- \rightleftharpoons 2\,Cl^-_{(aq)}$	+1.36
$BrO_3^- + 6\,H^+_{(aq)} + 6e^- \rightleftharpoons Br^-_{(aq)} + 3\,H_2O$	+1.44
$Ce^{4+}_{(aq)} + e^- \rightleftharpoons Ce^{3+}_{(aq)}$	+1.61
$Bk^{4+}_{(aq)} + e^- \rightleftharpoons Bk^{3+}_{(aq)}$	+1.67
$H_2O_{2\,(aq)} + 2\,H^+_{(aq)} + 2e^- \rightleftharpoons 2\,H_2O$	+1.77

In a review of previous experiments at REDC, instances of oxidized Bk ions not being adsorbed on *MP*-1 resin were discovered but this had been thought to be oxidation failure due to improper oxidation conditions. The presence of Ce in these current experiments helped to clarify these previous observations. Other studies indicated that this Bk (IV) behavior was observed early in 1967 at ORNL **[5]** but explained as being possibly the result of Bk (IV) instability and was succeeded by a simple separation of tracer Bk and Ce separation on Dowex-1 with $NaBrO_3$ (liquid) or PbO_2 (solid) as oxidizer. Since then, no complexation constant values were reported for Bk (IV), but one study by Makarova, et al **[6]** explored the possible reason of this Bk (IV) behavior with a comparative electromigration method. Electromigration of Bk (IV) and Ce (IV) in mixed HNO_3-$HClO_4$ solutions at $I = 6$ *M*, and of Bk (IV), Pu (IV), Th (IV), Ce (IV) in the HNO_3 range of 2~16

M showed that Bk (IV) in 3~6 *M* HNO_3 migrates as monovalent cations, e.g. $[Bk(H_2O)_X(NO_3)_3]^+$, but behaves as negatively charged ions only at ≥10*M* HNO_3. That well explained why Bk (IV) did not adsorb on *MP*-1 resins in 8 *M* HNO_3-$NaBrO_3$. It also suggested the possible formation of nitrate-complexed Bk (IV) anions in ≥10 *M* HNO_3 media.

The fact that only Ce(IV) adsorbed on *MP*-1 AX column and Bk (IV) did not was encouraging, rather than discouraging, since the removal of ^{141,144}Ce from ^{249}Bk by *MP*-1 resin column appears more efficient and complete than the originally planned process route: Cf removal on a *LN* resin column followed by selective eluting Ce off the column before Bk.

The different adsorption features of *MP*-1 and *LN* resins inspired a new processing route for purification of ^{249}Bk in the Bk Finishing step of the processing campaign.

DUAL COLUMN ARRANGEMENT FOR SEPARATING Bk FROM Cf AND Ce

In 8 *M* HNO_3-0.5 *M* $NaBrO_3$ media, the *MP*-1 resin column adsorbs Ce (IV) selectively, allowing Bk (IV) and Cf (III) to pass through the column, while the *LN* resin column adsorbs Bk (IV) selectively (in the absence of Ce), allowing Cf (III) to pass through the column.

These features of the two resins allow a new dual column arrangement to be designed for separating ^{249}Bk from impurities of Cf, Ce and non-rad impurities as follows:

1. Prepare one *MP*-1 resin column and one *LN* resin column and condition both with 8 *M* HNO_3-0.5 *M* $NaBrO_3$ solution. Prepare the feed (Bk, Cf, Ce and non-rad impurities) in a minimum volume of 8 *M* HNO_3-0.5 *M* $NaBrO_3$ solution, as well the 8 *M* HNO_3-0.5 *M* $NaBrO_3$ solution, prior to the column run.

2. Pass the feed/washes (both in 8 *M* HNO_3-0.5 *M* $NaBrO_3$) and 4 BV of 8 *M* HNO_3-0.5 *M* $NaBrO_3$ through the *MP*-1 resin column to adsorb ^{141,144}Ce selectively, and allow the *MP*-1 effluent (Bk, Cf, and non-rad impurities) to immediately enter the *LN* resin column to adsorb ^{249}Bk.

3. Put the *MP*-1 resin column (with Ce) aside for later treatment. The ^{141,144}Ce on *MP*-1 resin column can either simply be disposed with the column as solid waste or be stripped off the column with 0.15 *M* HNO_3-0.45 *M* H_2O_2 if the *MP*-1 column is to be re-used.

4. Continue adding 4~6 BV of 8 *M* HNO_3-0.5 *M* $NaBrO_3$ onto the *LN* resin column to elute Cf and non-rad metal ions completely from the column, while ^{249}Bk continue to be adsorbed on the column. Add 2 BV of 0.15~4 *M* HNO_3 to remove $NaBrO_3$ from the resin bed, then add 4~6 BV of 4~8 *M* HNO_3-0.45 *M* H_2O_2 to strip Bk off the *LN* resin column.

A dual column of *MP*-1/*LN* was fabricated to increase operational efficiency, as shown in **Fig. 8**:

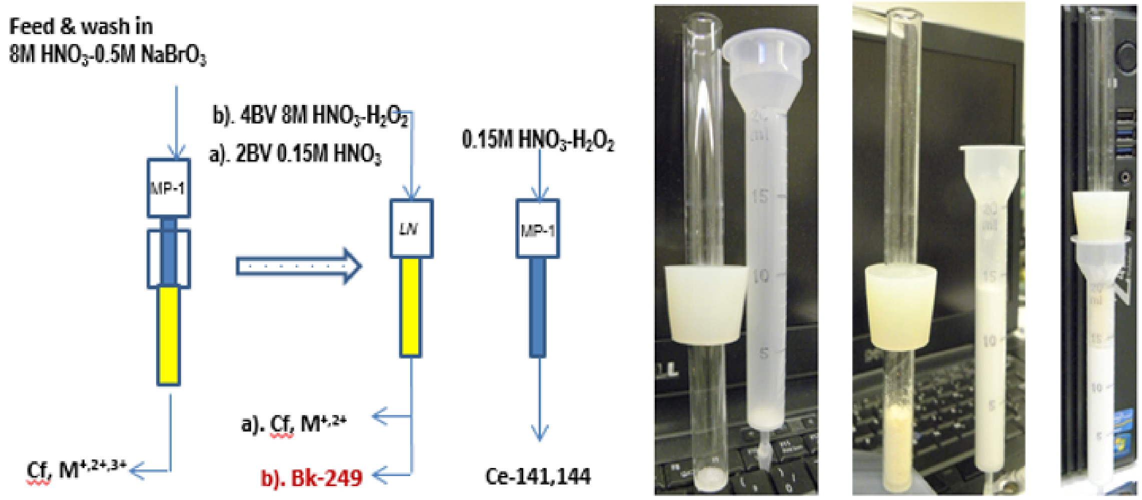


Fig 8 Dual column set-up and its operations for ^{249}Bk purification

Replace the current Bk Finishing (BERKEX and Glove-box AHIB process) with the new dual column method (the dual column can be operated twice if needed), as shown in **Fig. 9**:

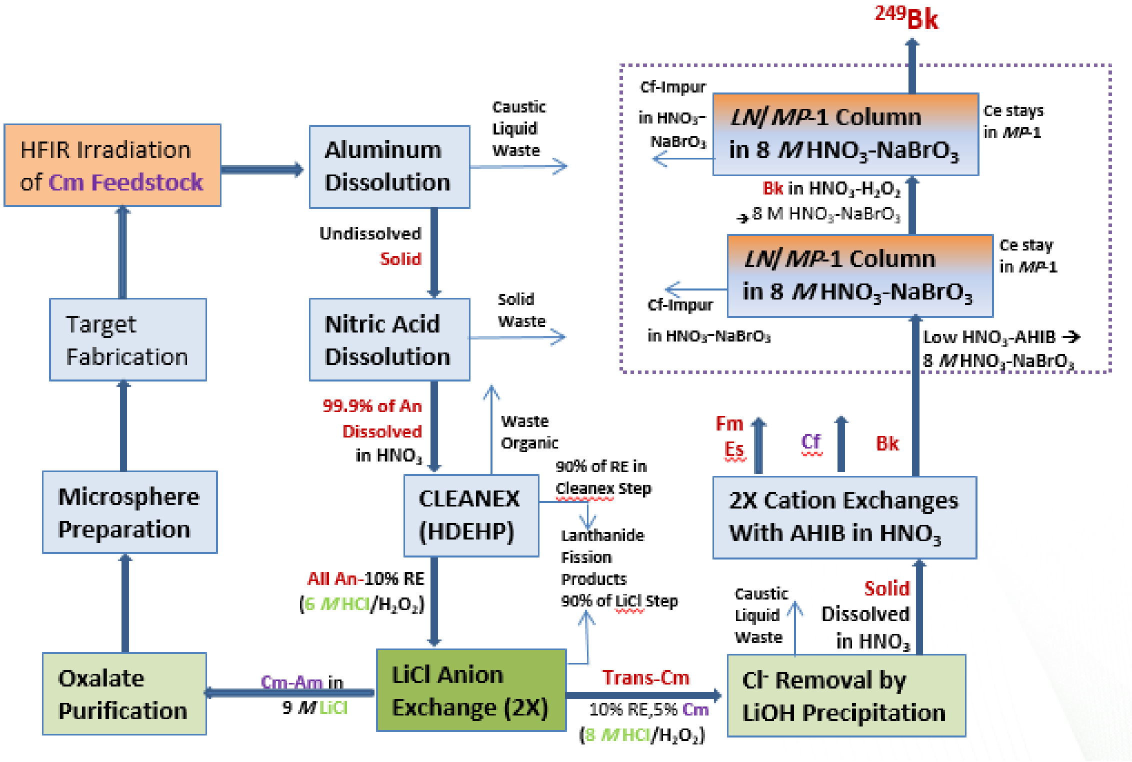


Fig 9 The post-irradiation processing steps after implimentation of the dual column method

The benefits of using the new dual column method include

1. Bk Finishing is expected to be completed within three weeks, compared with previous BERKEX and glove-box AHIB processing, which required ≥ 3 months. Feed preparation is simple for a dual column run. The 80 mL of feed in 8 M HNO_3-0.5 M $NaBrO_3$ needs only one additional CX column run for AHIB removal and one matrix adjustment for acidity/[BrO_3^-] if the treated solution is the fraction directly from the hot cell AHIB operation. This method eliminates many preparatory steps required by the BERKEX/glove-box AHIB process, including triple extraction by trichloroethylene (TCE) for dodecane removal, solution drying down from 500 mL to 1 mL, and the AHIB removal column run for the final product solution.

2. Operations are much simpler: room temperature for column runs instead of 73°C; gravity flow rate with no control by counting drops per second; no delicate pH

adjustment of the effluents; “cut off” type column use with no chromatographic separation on the same column.

3. The higher ^{249}Bk recovery and Cf removal are promising, plus no organic liquid waste (HDEHP) is generated by this method.

POSSIBILITIES OF USING THE DUAL COLUMN METHOD AHEAD OF BK FINISHING

The dual column method extracts Bk (IV) by itself and the column scale can be easily enlarged to accommodate higher throughput requirements, as are expected in campaign processing steps ahead of the current Bk Finishing process. Of course, the sooner the ^{249}Bk is extracted, the higher the ^{249}Bk production in terms of reduced decay loss.

Use of the dual column method earlier in the processing campaign may lead to other issues to be studied or resolved. If it is used immediately after Acid Dissolution (ahead of CLEANEX), for example, the radiation doses for the resins and oxidizer will be millions of times higher from FPs than in the Bk Finishing step. Whether BrO_3^- will be able to complete its oxidization function is questionable, although other oxidizer candidates (e.g. CrO_3) are available. For another example, if the method is used immediately after LiCl Anion Exchange, the feed of the dual columns is in a HCl medium. In that case, BrO_3^- will be consumed due to oxidation of Cl^- (see **Table-1**), although CrO_3 may be working well as a substitute oxidizer. Hence, additional experiments need to be conducted to investigate these possibilities.

More importantly, ^{252}Cf is the heavy element product of primary interest in the current processing campaigns because of its importance in industrial and research applications. It will take an important administrative decision to allow extraction of ^{249}Bk ahead of ^{252}Cf, leaving the “contaminant” BrO_3^- in the Cf processing stream, even though removal of BrO_3^- takes only a short period of heating.

The more revolutionary production route for ^{249}Bk will be a ^{249}Bk-specific production campaign using enriched ^{248}Cm (not Cm feedstock) as the irradiation target (requiring only 1~2 irradiation cycles and a 30-day cooling period). A “Thermal Neutron Filter” technique will be applied in target fabrication to greatly reduce ^{249}Bk "burn-up", in hopes of tripling the ^{249}Bk yield at reactor discharge. The dual column method will be used directly on the dissolved target material for ^{249}Bk extraction and purification in a much shorter post-irradiation processing campaign.

Conclusions

A new dual column method has been developed for the Bk Finishing process, in support of heavy element production campaign, for selectively separating and purifying ^{249}Bk from other trans-Cm elements and FP impurities. This method greatly shortens the processing period with fewer operation steps and simpler operational controls. Higher recovery of ^{249}Bk per campaign can be achieved with this revised processing route, since decay loss is reduced due to a shorter post-irradiation processing.

To satisfy an increasing demand of ^{249}Bk, a campaign is needed specifically aimed at the production of ^{249}Bk using enriched ^{248}Cm as an irradiation target and the "Thermal Neutron Filter" technique to reduce ^{249}Bk "burn-up" during target irradiation. The lower yield of FP impurities and less complicated target components of the campaign would allow the dual column method to be used for direct separation of ^{249}Bk from the target solution immediately after the Acid Dissolution step.

Additional research and testing will be required to determine whether this dual-column method of extracting ^{249}Bk can be used in the early steps of the current multistep processing campaign.

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Dr. Susan Hogle, for communications concerning her research project of "Thermal Neutron Filter" technique.

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Supplementary information

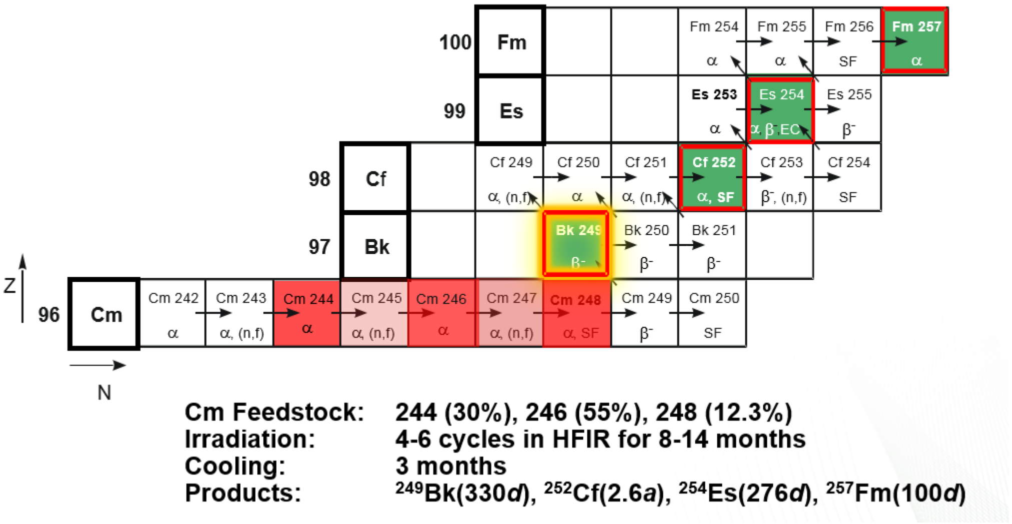


Fig 1 ^{249}Bk produced by multiple neutron captures and beta decays of irradiated Cm feedstock

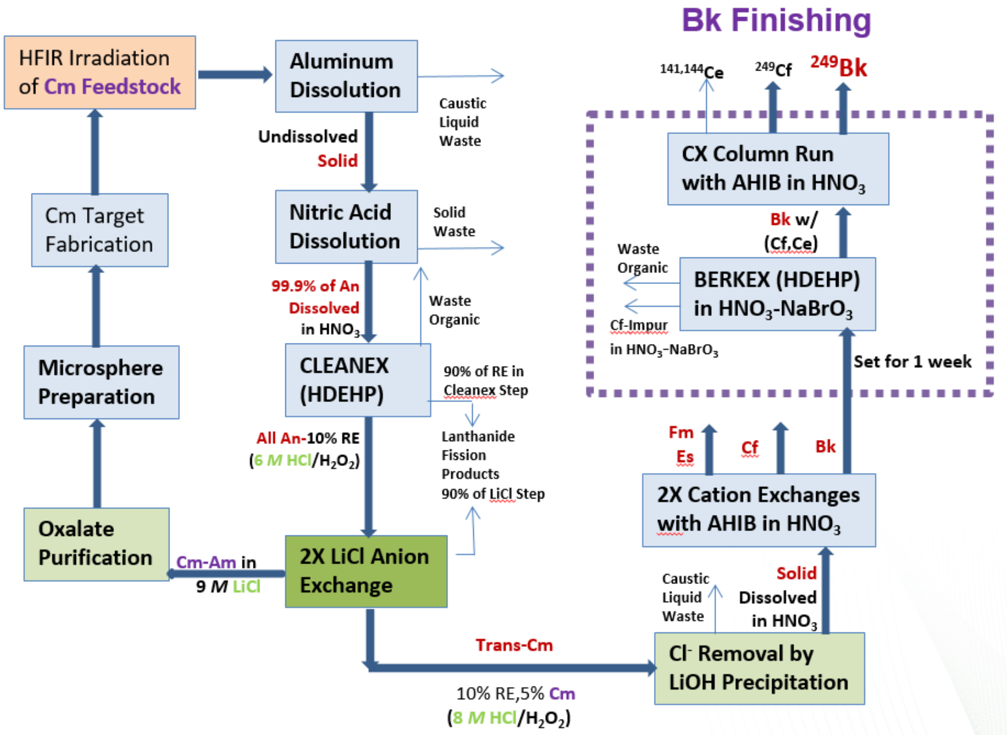
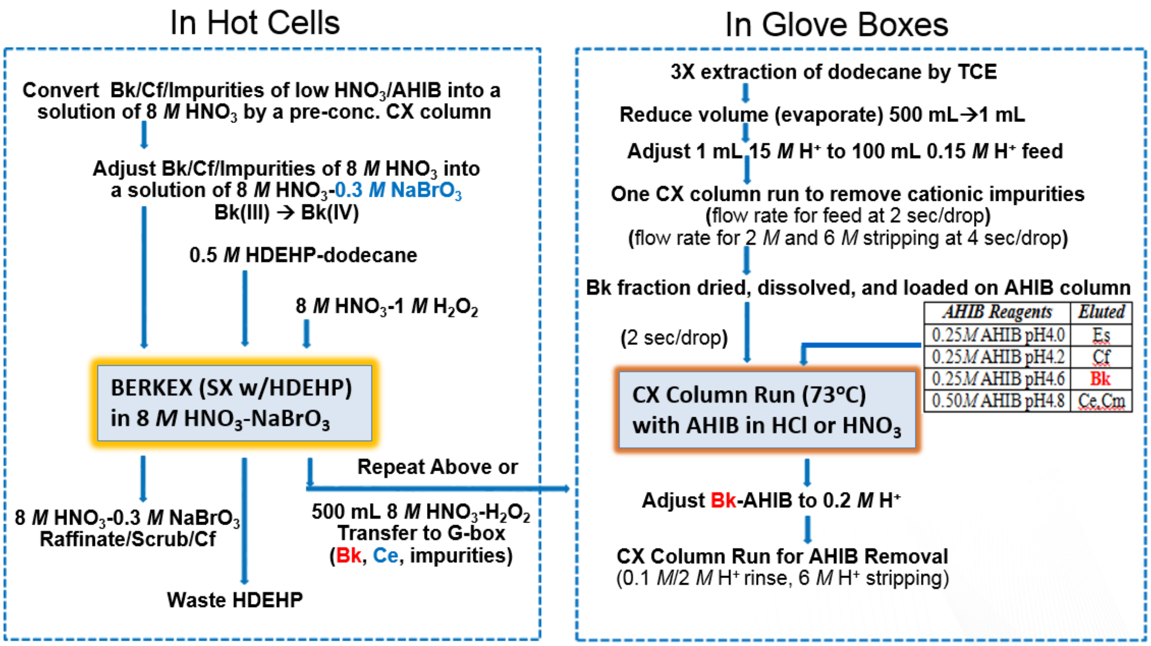
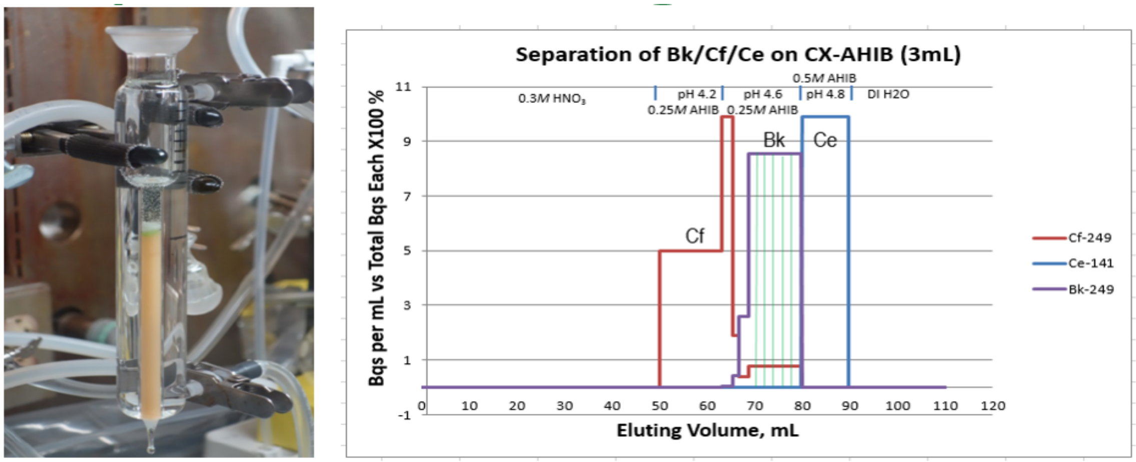


Fig 2 Major steps of the post-irradiation processing of an irradiated Cm feedstock target



AHIB Reagents	*Eluted*
0.25M AHIB pH4.0	Es
0.25M AHIB pH4.2	Cf
0.25M AHIB pH4.6	Bk
0.50M AHIB pH4.8	Ce,Cm

Fig 3 Major operation steps of BERKEX in a hot cell and AHIB in a glove box



3 mL column: Dowex 50W X8 Resin (73°C)

Adjust berkelium solution to 0.1 M HCl

Add ~8 CV 0.3 M NH_4NO_3 (convert resin)

Add ~2 CV water to remove nitrates

Add ~4 CV 0.25 M pH 4.2 AHIB (Cf)

Add ~5 CV 0.25 M pH 4.6 AHIB (Bk)

Add ~3 CV 0.25 M pH 4.8 AHIB (Ce)

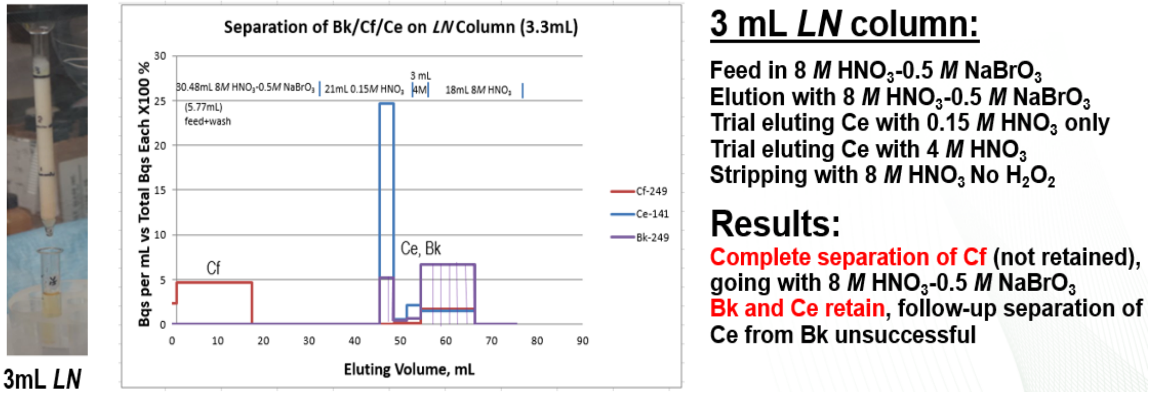
Feed:

7.22E11 Bq ^{249}**Bk** 13 mg
9.75E7 Bq ^{249}**Cf** 8.5 µg
1.70E7 Bq ^{141}**Ce** 1.6E-4 µg
Components normalized to 1
with **Y axis for % distribution**

^{249}Bk Product:

6.78E11 Bq ^{249}**Bk** (93.9%)
4.04E6 Bq ^{249}**Cf** (4.1%)
No ^{141}**Ce** in shipped product

Fig 4 Details of the glove box operations of the AHIB column run in Campaign-77



3 mL *LN* column:

Feed in 8 *M* HNO_3-0.5 *M* $NaBrO_3$
Elution with 8 *M* HNO_3-0.5 *M* $NaBrO_3$
Trial eluting Ce with 0.15 *M* HNO_3 only
Trial eluting Ce with 4 *M* HNO_3
Stripping with 8 *M* HNO_3 No H_2O_2

Results:

Complete separation of Cf (not retained), going with 8 *M* HNO_3-0.5 *M* $NaBrO_3$
Bk and Ce retain, follow-up separation of Ce from Bk unsuccessful

Fig 5 The elution profile of *LN* (3.3 mL) resin column run

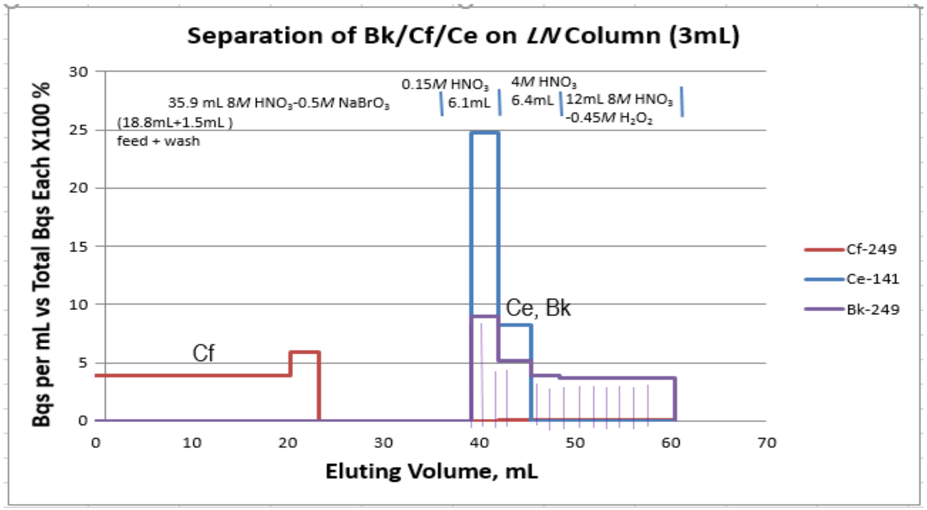
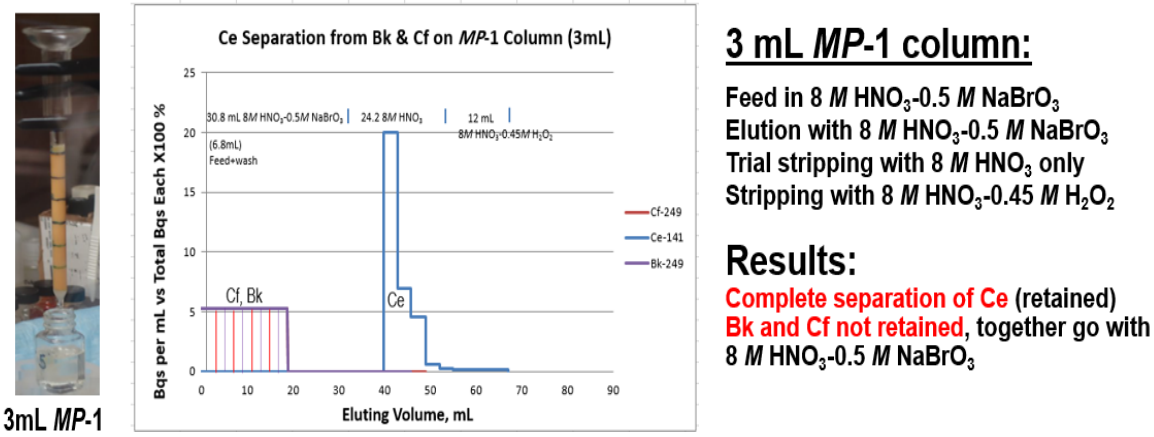


Fig 6 The elution profile of the second *LN* resin column (3 mL) run



3 mL *MP*-1 column:

Feed in 8 *M* HNO_3-0.5 *M* $NaBrO_3$
Elution with 8 *M* HNO_3-0.5 *M* $NaBrO_3$
Trial stripping with 8 *M* HNO_3 only
Stripping with 8 *M* HNO_3-0.45 *M* H_2O_2

Results:

Complete separation of Ce (retained)
Bk and Cf not retained, together go with 8 *M* HNO_3-0.5 *M* $NaBrO_3$

Fig 7 The elution profile of the *MP*-1 resin column (3 mL) run

Table-1 Standard reduction potentials (E^o) of concerned ions

Half-Reactions	***Eº (V)***
$O_{2\,(g)} + 2\,H^+_{(aq)} + 2e^- \rightleftharpoons H_2O_{2\,(aq)}$	+0.68
$Br_{2\,(l)} + 2e^- \rightleftharpoons 2\,Br^-_{(aq)}$	+1.07
$Cr_2O_7^{2-}{}_{(aq)} + 14\,H^+_{(aq)} + 6e^- \rightleftharpoons 2\,Cr^{3+}_{(aq)} + 7\,H_2O$	+1.33
$Cl_{2\,(l)} + 2e^- \rightleftharpoons 2\,Cl^-_{(aq)}$	+1.36
$BrO_3^- + 6\,H^+_{(aq)} + 6e^- \rightleftharpoons Br^-_{(aq)} + 3\,H_2O$	+1.44
$Ce^{4+}_{(aq)} + e^- \rightleftharpoons Ce^{3+}_{(aq)}$	+1.61
$Bk^{4+}_{(aq)} + e^- \rightleftharpoons Bk^{3+}_{(aq)}$	+1.67
$H_2O_{2\,(aq)} + 2\,H^+_{(aq)} + 2e^- \rightleftharpoons 2\,H_2O$	+1.77

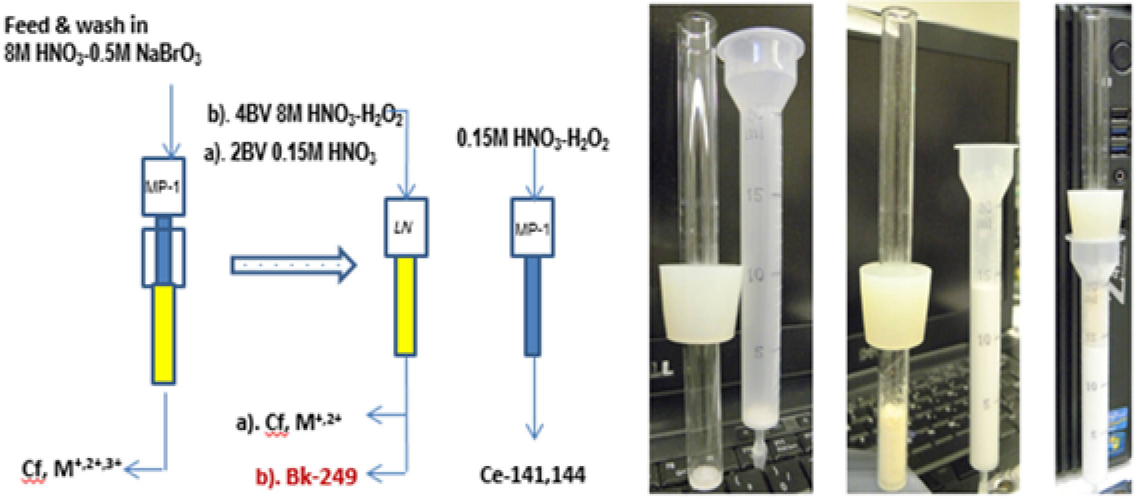


Fig 8 Dual column set-up and its operations for ^{249}Bk purification

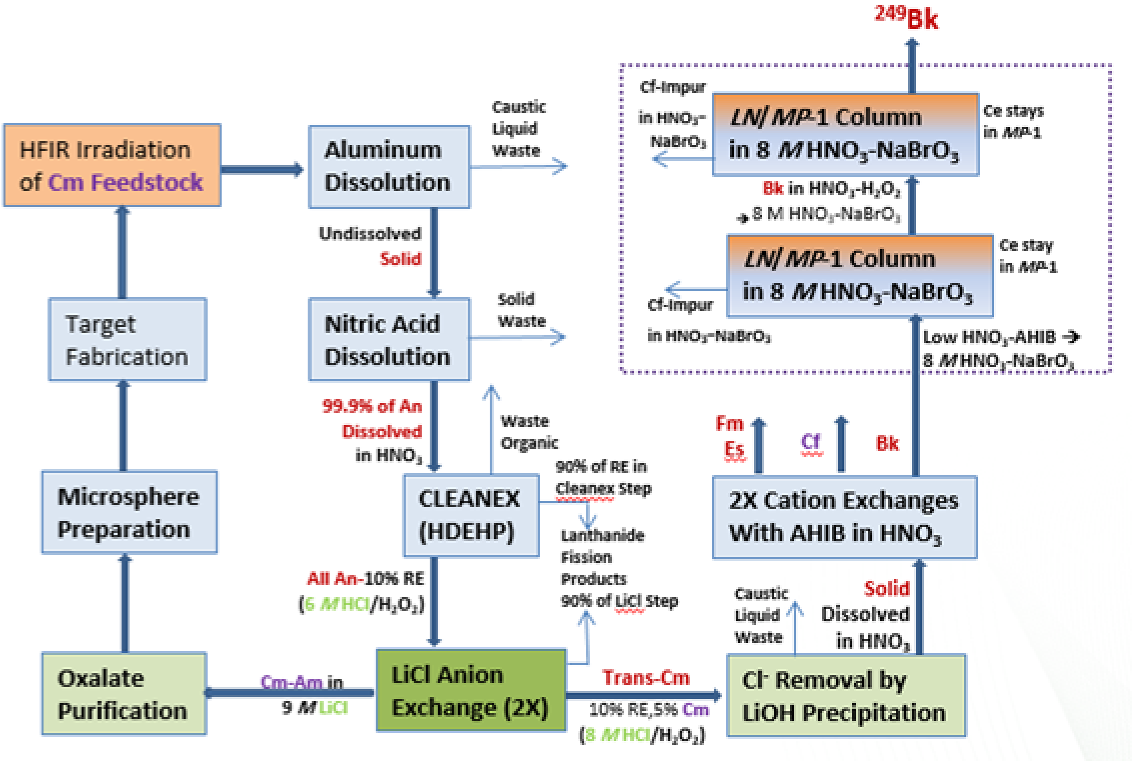


Fig 9 The post-irradiation processing steps after implimentation of the dual column method