

# Application of a Dual-Column Method to Selectively Extract and Purify Berkelium-249 from Other Actinides and Impurities



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September 2019

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Nuclear Security and Isotope Technology

**APPLICATION OF A DUAL-COLUMN METHOD TO SELECTIVELY EXTRACT  
AND PURIFY BERKELIUM-249 FROM OTHER ACTINIDES AND IMPURITIES**

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September 2019

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## ACRONYMS

AHIB	$\alpha$ -hydroxyisobutyrate
An	actinides
AX	anion exchange
BG	background
Bq	becquerel
BV	bed volume
C-77	Campaign-77
CX	cation exchange
DI	deionized
DOE	US Department of Energy
FP	fission products
HDEHP	di-(2-ethylhexyl) phosphoric acid
HFIR	High Flux Isotope Reactor
HPGe	high-purity germanium
ID	internal diameter
I/D	length/diameter
LN	Eichrom extraction resin name
Ln	lanthanides
mL	milliliters
MP-1	anion exchange resin name
ORNL	Oak Ridge National Laboratory
pH	$-\log [\text{H}^+]$ (hydrogen concentration)
REDC	Radiochemical Engineering Development Center
SX	solvent extraction
TCE	trichloroethylene

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## ABSTRACT

The super-heavy element tennessine (Ts, element 117) was discovered in 2016 by a collaboration of US and Russian scientists via bombardment reaction of  $^{249}\text{Bk} + ^{48}\text{Ca} \rightarrow ^{117}\text{Ts}$ . The target element  $^{249}\text{Bk}$  (half-life 330d) was produced and provided by the Radiochemical Engineering Development Center (REDC) at Oak Ridge National Laboratory (ORNL). The production of  $^{249}\text{Bk}$  at REDC requires a multi-step chemical process using an irradiated curium feedstock target to remove all fission product elements and to separate  $^{249}\text{Bk}$  from other actinide elements (Am, Cm, Cf, Fm, and Es). The process includes Caustic Dissolution, Acid Dissolution, Cleanex, two LiCl Anion Exchanges, LiOH Precipitation, Cation Exchange with  $\alpha$ -hydroxy isobutyric acid (AHIB), and Bk Finishing as the final Bk purification step. The major product of this campaign is  $^{252}\text{Cf}$ , while  $^{249}\text{Bk}$  is one of the important by-products. The current Cf campaign for recovery of approximately 15 mg of  $^{249}\text{Bk}$  per campaign (not including the time for finishing of Cf, Fm, and Es) takes 6 or 7 months, including  $\sim 3$  months spent on Bk Finishing.

Berkelium Finishing includes two major processes: (1) BERKEX, operated inside a hot cell with two cycles of batch solvent extraction using di-2-ethylhexyl phosphoric acid (HDEHP) as the extractant for tetravalent  $^{249}\text{Bk}$  from an 8 M  $\text{HNO}_3$ -0.3 M  $\text{NaBrO}_3$  solution and (2) cation exchange with AHIB, operated inside a glove box laboratory. The entire Bk Finishing process takes five solvent extractions, more than five column runs, and several drying processes for aqueous solutions, including one from 500 mL to 1 mL for volume reduction. To shorten the Bk Finishing period and simplify the Bk purification operation steps, the possibility of using other resin columns was explored.

Recent trials using columns of either *LN* resin or *MP*-1 anion exchange resin to adsorb the tetravalent  $^{249}\text{Bk}^{4+}$  in 8 M  $\text{HNO}_3$ -0.5 M  $\text{NaBrO}_3$ , followed by elution of impurities (e.g.  $\text{Ce}^{4+}$ ,  $\text{Cf}^{3+}$ ) and stripping of  $^{249}\text{Bk}$ , resulted in a new dual-column method of selectively separating  $^{249}\text{Bk}$  from other trans-plutonium elements and fission product impurities. This new method is proposed to replace the current Bk Finishing process to provide increased Bk purification efficiency and a shorter processing period of 4 to 5 months (resulting in less decay loss for a higher  $^{249}\text{Bk}$  production). This report discusses the experimental results, describes the dual-column method with relevant redox chemistry issues, and several possible options for its use in further process steps preceding Bk Finishing.



# 1. INTRODUCTION

The demand for heavy trans-plutonium target materials, including  $^{249}\text{Bk}$  (half-life 330 *d*), by the super-heavy element research community is increasing, but production of these elements requires complex multi-step campaigns. Berkelium-249 is produced via a series of 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). Figure 1 shows the nuclear reaction route used to produce  $^{249}\text{Bk}$  in HFIR, and Figure 2 shows the major post-irradiation processing steps after target discharge from the reactor and cooling.

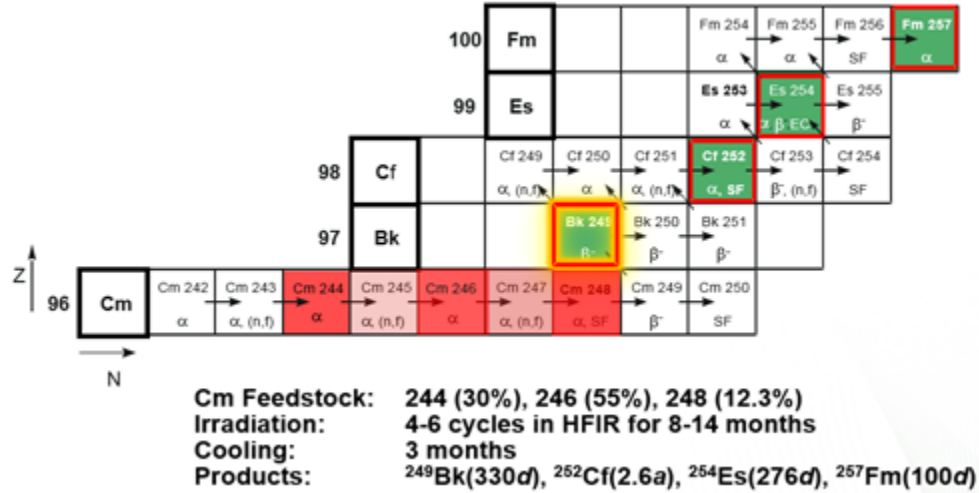


Figure 1.  $^{249}\text{Bk}$  produced by neutron captures and beta decays of irradiated Cm feedstock.

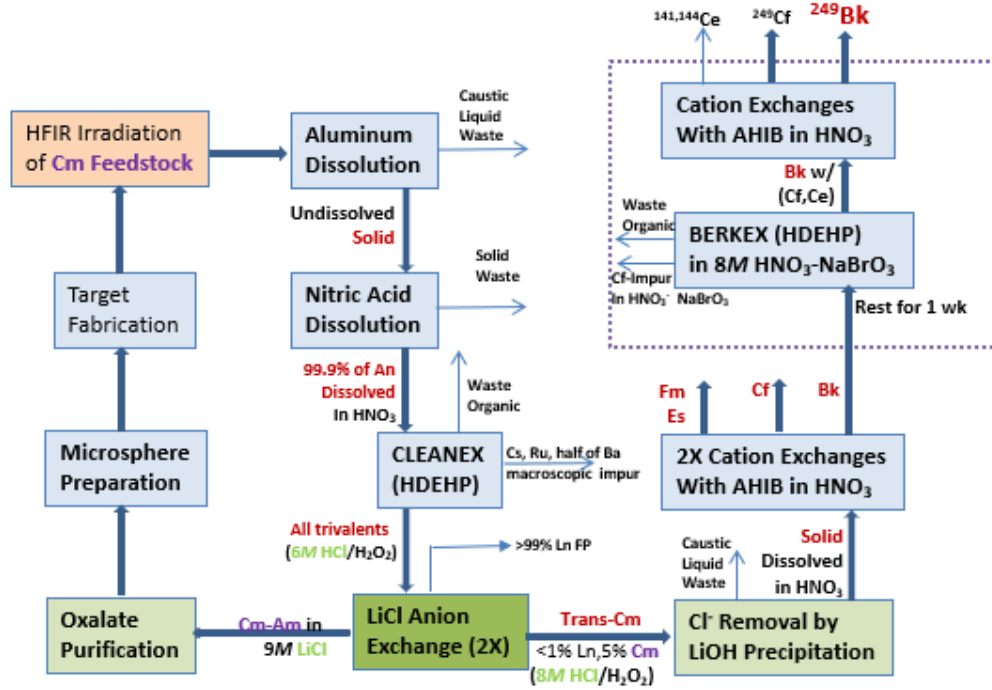
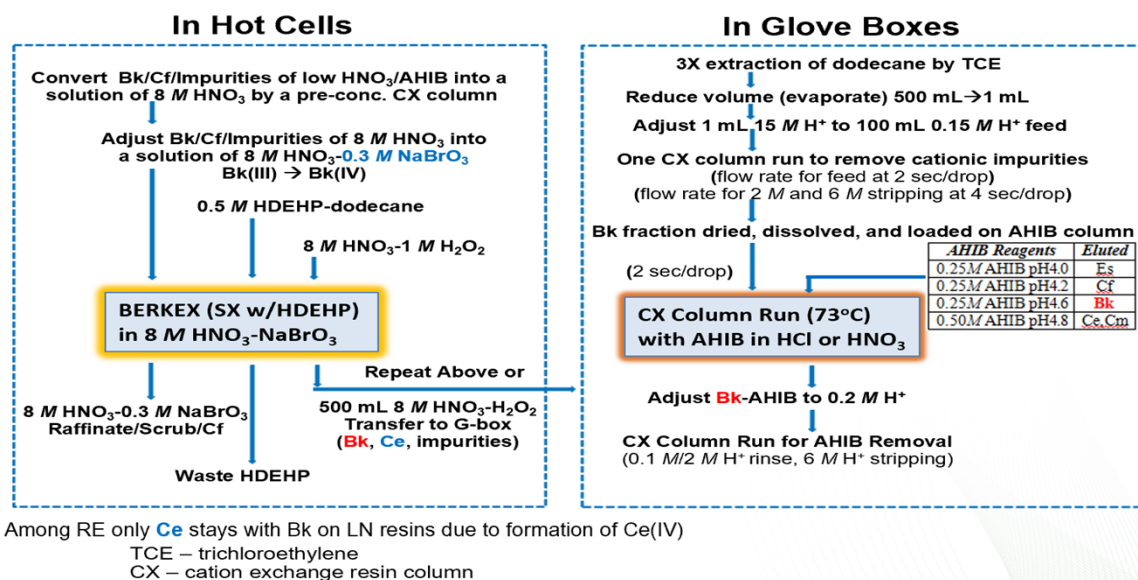


Figure 2. Major steps of the post-irradiation processing of the irradiated Cm feedstock target.

The direct nuclear reaction route for  $^{249}\text{Bk}$  production in HFIR is neutron capture by  $^{248}\text{Cm}$  followed by a  $\beta^-$  decay, i.e.  $^{248}\text{Cm} (n, \gamma) ^{249}\text{Cm} \xrightarrow{\beta^- (1.07\text{ h})} ^{249}\text{Bk}$ . The  $^{248}\text{Cm}$  content in current Cm feedstock targets is only 12%, which limits the peak yield of  $^{249}\text{Bk}$  per target by irradiation. The peak yield of  $^{249}\text{Bk}$  is approached by first cycle of irradiation at HFIR; additional irradiation cycles result in  $^{249}\text{Bk}$  “burnup” to produce heavier elements (e.g.  $^{252}\text{Cf}$ ,  $^{254}\text{Es}$ , and  $^{257}\text{Fm}$ ), because the major product of the Cf campaign process is  $^{252}\text{Cf}$ , while other trans-curium isotopes, including  $^{249}\text{Bk}$ , are considered as by-products. Four to approximately six cycles of irradiation also require a longer cooling period of 3 months.

Post-irradiation chemical processing requires a multi-step process. Caustic Dissolution dissolves and removes the aluminum in irradiated aluminum-matrix cermet targets and their aluminum cladding. Acid Dissolution dissolves the target core material into an acidic solution. The CLEANEX process extracts and purifies trivalent actinides (An) and lanthanide (Ln) fission products (FPs) from common macroscopic non-trivalent contaminants in the dissolved irradiated Cm feedstock targets. Two LiCl anion exchange (AX) processes remove Ln FPs from all actinides (An) and then separate Cm-Am from trans-curium isotopes, which include  $^{249}\text{Bk}$ ,  $^{252}\text{Cf}$ ,  $^{254}\text{Es}$ , and  $^{257}\text{Fm}$ . The primary separation of  $^{249}\text{Bk}$  from other trans-Cm isotopes is accomplished via cation exchange (CX) with  $\alpha$ -hydroxyisobutyrate (AHIB) in a hot cell. Berkelium Finishing, the final purification step for the  $^{249}\text{Bk}$  product, removes all other residual impurities from  $^{249}\text{Bk}$ .

Berkelium Finishing includes two major processes (BERKEX and CX-AHIB), as shown in Figure 3: BERKEX: solvent extraction (SX) with di-(2-ethylhexyl) phosphoric acid (HDEHP)-dodecane in an 8 M  $\text{HNO}_3$ -0.3 M  $\text{NaBrO}_3$  solution inside a hot cell, and CX-AHIB: CX column runs with AHIB in a glove box. In the BERKEX process,  $\text{Bk}^{3+}$  is oxidized to  $\text{Bk}^{4+}$  by  $\text{BrO}_3^-$  and extracted by HDEHP in 8 M  $\text{HNO}_3$  ( $\text{Ce}^{4+}$ , an oxidized Ln FP, is also extracted by HDEHP), while impurities of  $\text{M}^+$ ,  $\text{M}^{2+}$  and  $\text{M}^{3+}$  remain in an aqueous phase. Extracted  $\text{Bk}^{4+}$  and  $\text{Ce}^{4+}$  in HDEHP organic phase is later back-extracted into 8M  $\text{HNO}_3$ -0.45M  $\text{H}_2\text{O}_2$  to achieve Bk separation from the majority of impurities. After two cycles of BERKEX runs, a raw Bk fraction in 500 mL of 8 M  $\text{HNO}_3$ -0.45 M  $\text{H}_2\text{O}_2$  is produced and transferred to a glove box for further purification by CX AHIB runs.



**Figure 3. Major operation steps of BERKEX in hot cell and CX with AHIB in glove box labs.**

Glove box AHIB operations include residual organic (HDEHP-dodecane) removal (three SXs with trichloroethylene [TCE]) and three CX resin column runs: one is for pre-concentrating all cations to



prepare the feed for the CX AHIB column run; a second is the AHIB column run itself for final purification of  $^{249}\text{Bk}$ ; the third is for AHIB removal from the  $^{249}\text{Bk}$  product cut of the AHIB run. The AHIB column run employs AHIB as a competing ligand ( $\text{COO}^-$ ) in the mobile phase to compete with the ability of the CX resin ( $\text{SO}_3^-$ ) to adsorb cations. Increasing the pH and/or AHIB concentration results in actinides on the CX column to be eluted in the order of their charge densities (for actinides of the same valence, in order of their ion sizes:  $\text{Fm}^{3+}$ ,  $\text{Es}^{3+}$ ,  $\text{Cf}^{3+}$ , and then  $\text{Bk}^{3+}$ ). The operation of CX-AHIB column requires strict control of pH, flow rate, and column temperature, together with careful segmentation of the effluent. Because the Bk and Cf peaks are very close in AHIB column run, a small portion of Cf peak tails may be collected in the  $^{249}\text{Bk}$  product cut.

Figure 4 provides 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 ( $73^\circ\text{C}$ ), pH (4.2, 4.6, and 4.8), and flow rate (counting seconds/drop) with an argon pressure regulator. The “fraction cut of  $^{249}\text{Bk}$  product” (the shaded portion) in the AHIB run of C-77 achieved 94% recovery of  $^{249}\text{Bk}$  from the feed, but with 4.1% of  $^{249}\text{Cf}$  carried over from the feed. (These were the percentages after deducting the sample ingrowth of  $^{249}\text{Cf}$  [half-life 351 years] due to  $^{249}\text{Bk}$  decay during the 27.5 hours from sample collection to activity analyses.)

*Note: The y-axes of all elution plots in this paper are in Bq/mL vs. each isotope's total Bq and are expressed as a percentage distribution of each isotope (normalized to 1) with the same peak areas as 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 the productivity of  $^{249}\text{Bk}$  recovery by shortening the processing time, two kinds of resins were tested with a feed from combined fractions of the C-77 glove box CX-AHIB run (except for the product fraction with 13 mg of  $^{249}\text{Bk}$ ): Eichrom LN resins and BioRad MP-1 AX resins.

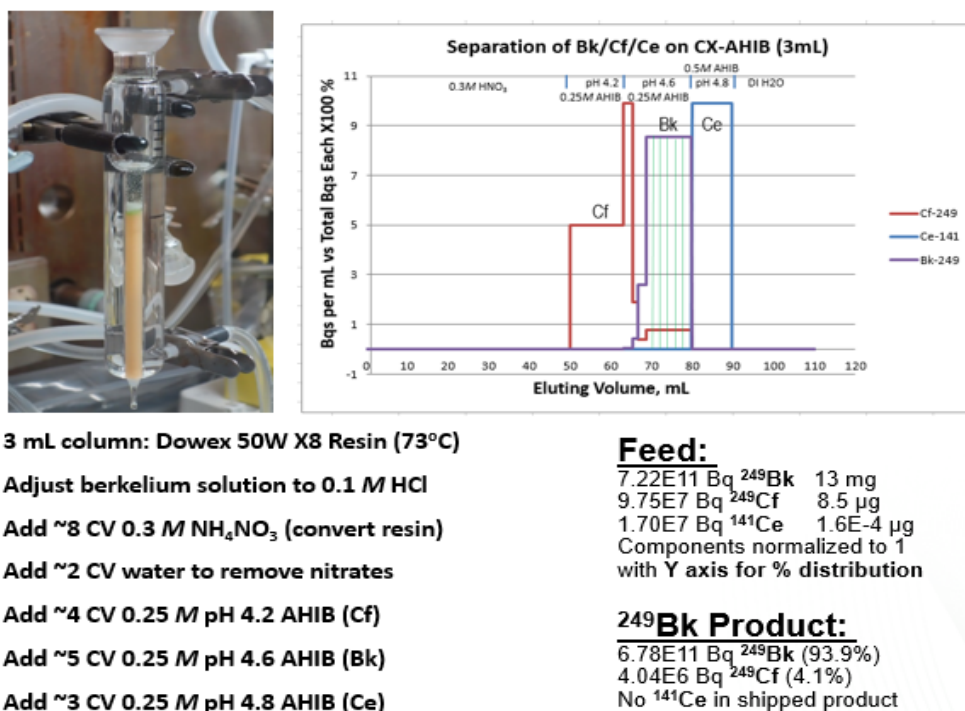


Figure 4. Details of the glove box operation of the AHIB column run in Campaign-77.

## 2. EXPERIMENTAL

### 2.1 REAGENTS, RESINS, AND RADIONUCLIDES

Nitric acid (69–70% ACS grade  $\text{HNO}_3$ ) was purchased from Fisher Chemical, and 2  $M$   $\text{NaBrO}_3$  was prepared with solid  $\text{NaBrO}_3$  of 99+% purity purchased from ACROS Organics. The Bio Rad *MP*-1 resin (chloride form) with a particle size of 100–200 mesh was purchased from BioRad. The Eichrom *LN* resin with a particle size of 100–150  $\mu$  was purchased from Eichrom. 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 the  $^{249}\text{Bk}$  product), that were passed through the CX resin to remove AHIB. This radionuclide stock solution contained  $2.6 \times 10^{10}$  Bq (0.4 mg) of  $^{249}\text{Bk}$ ,  $9.75 \times 10^7$  Bq (8.5  $\mu\text{g}$ ) of  $^{249}\text{Cf}$ ,  $4.44 \times 10^6$  Bq (0.22  $\mu\text{g}$ ) of  $^{252}\text{Cf}$ ,  $1.7 \times 10^7$  Bq (ca.  $1.6 \times 10^{-4}$   $\mu\text{g}$ ) of  $^{141,144}\text{Ce}$ , and other non-rad impurities.

### 2.2 PREPARATION OF FEED AND ELUTING SOLUTIONS

Addition of  $\text{NaBrO}_3$  into  $\text{HNO}_3$  for either feed or elution solutions of 8  $M$   $\text{HNO}_3$ -0.5  $M$   $\text{NaBrO}_3$  is required 20–30 minutes before use, in order to minimize the  $\text{BrO}_3^-$  reduction to  $\text{Br}^-$  or  $\text{Br}_2$  (the color of the solutions turned orange). The elution solution of 8  $M$   $\text{HNO}_3$ -0.5  $M$   $\text{NaBrO}_3$  was prepared by mixing a stock of 10.67  $M$   $\text{HNO}_3$  with a stock of 2  $M$   $\text{NaBrO}_3$  in a volume ratio of 3:1 (only 20–30 minutes before use). The stock solution of radionuclides was also prepared in 10.67  $M$   $\text{HNO}_3$ . The feed solution of any desired volumes was prepared by mixing the stock of radionuclides of 10.67  $M$   $\text{HNO}_3$  with the stock of 2  $M$   $\text{NaBrO}_3$  in a volume ratio of 3:1 (only 20–30 minutes before use). Other  $\text{HNO}_3$  solutions were prepared by using 15  $M$   $\text{HNO}_3$  diluted with deionized (DI)  $\text{H}_2\text{O}$  to the desired  $\text{HNO}_3$  concentrations. An 8  $M$   $\text{HNO}_3$ -0.45  $M$   $\text{H}_2\text{O}_2$  solution was prepared as a stock solution every other day.

### 2.3 COLUMN PREPARATION

Glass columns of the same dimensions and same 3.0 mL resin bed volume (BV) as those of the AHIB column were chosen for the *MP*-1 and the *LN* column runs. Both the *MP*-1 resin and the Eichrom *LN* resin were pre-wetted in DI  $\text{H}_2\text{O}$  and packed in two glass columns with internal diameters (IDs) of 0.6 cm up to the 3 mL BV mark (the first *LN* column was accidentally assembled up to the 3.3 mL). The resin bed heights of the columns (3.0 mL) were 10.5 cm, so the same length-to-diameter (L/D) ratio of 17.5 was used for both columns in the experiments. Before and after resin loading, quartz wool was put into the tops of the columns to avoid resin leaking and was placed atop the resin beds to prevent the resin from mixing. The columns were assembled and pre-conditioned with enough 8  $M$   $\text{HNO}_3$  outside the glove box and then conditioned with  $\geq 3$  BV of 8  $M$   $\text{HNO}_3$ -0.5  $M$   $\text{NaBrO}_3$  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.

### 2.4 OPERATIONS OF COLUMN RUNS

Each 8  $M$ - $\text{HNO}_3$ -conditioned resin column, after bagging in a glove box, needed to be conditioned with a  $\geq 3$  BV of 8  $M$   $\text{HNO}_3$ -0.5  $M$   $\text{NaBrO}_3$  solution before use. The feed solution for each column run was prepared by adding 2  $M$   $\text{NaBrO}_3$  to the aliquots of the stock radionuclide of 10.67  $M$   $\text{HNO}_3$  in a volume ratio of 1:3 and mixing by shaking. The feed solution was allowed to stand for 20–30 minutes to ensure complete oxidation of  $^{249}\text{Bk}$ .

The *LN* resin column (3.3 mL) run and *MP*-1 resin column (3.0 mL) run each used half of the aforementioned stock solution of radionuclides as a 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 the feed was loaded, three or more washes (8  $M$   $\text{HNO}_3$ -0.5  $M$   $\text{NaBrO}_3$ ) of the vial of radionuclide stock were added to the column.

Then, the eluting solution of 8 M HNO<sub>3</sub>–0.5 M NaBrO<sub>3</sub> was added to the column. This portion of feed + washes + elution with 8 M HNO<sub>3</sub>–0.5 M NaBrO<sub>3</sub> was presumed to be a collection of radionuclides without the <sup>249</sup>Bk product.

In the first *LN* run, the portion of 8 M HNO<sub>3</sub>–0.5 M NaBrO<sub>3</sub> was 9.2 BV, including 1.7 BV of feed/washes. In the *MP*-1 run, the portion of 8 M HNO<sub>3</sub>–0.5 M NaBrO<sub>3</sub> was 10 BV, including 2.3 BV of feed/washes. In the second *LN* run, the portion of 8 M HNO<sub>3</sub>–0.5 M NaBrO<sub>3</sub> was 11 BV, including 6.8 BV of feed/washes. After column elution with 8 M HNO<sub>3</sub>–0.5 M NaBrO<sub>3</sub>, various solutions were used for stripping <sup>249</sup>Bk off or selectively eluting <sup>141,144</sup>Ce off the column.

## 2.5 SAMPLE ANALYSIS

The Analytical Group at the Radiochemical Engineering Development Center (REDC) of ORNL is well equipped with a variety of radiological analysis instrumentation, including HPGe gamma spectrometers, alpha spectrometers (PIPS detectors), and an inductively coupled plasma-mass spectrometer (Thermo Fisher iCAP Q). Because the REDC liquid scintillation counter was temporarily unavailable, samples of <sup>249</sup>Bk were measured using a gas-flow proportional counter based on calibrations made with a <sup>249</sup>Bk sample pre-measured by a PerkinElmer 5110TR liquid scintillation counter. Samples of <sup>249</sup>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 and 388.3 keV. Samples of <sup>141,144</sup>Ce were measured using a gamma spectrometric method, based on their typical gamma energies of 145.4 keV (<sup>141</sup>Ce) and 133.5 keV (<sup>144</sup>Ce). Some of the samples of <sup>249</sup>Cf and <sup>141,144</sup>Ce were measured using a GMX-25 coaxial HPGe gamma spectrometer, based on typical gamma energies in a relatively high-background lab environment.

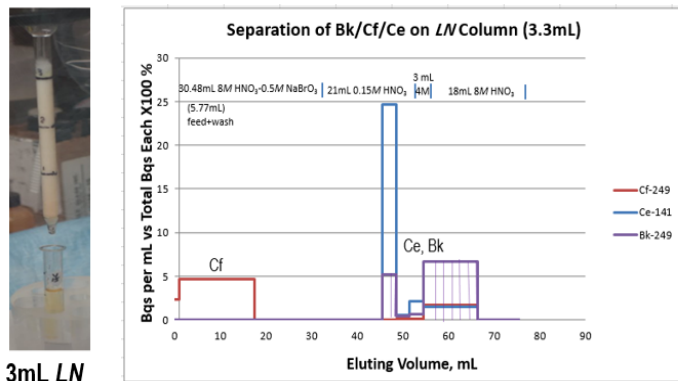
## 3. RESULTS AND DISCUSSION

### 3.1 EICHROM *LN* RESIN COLUMNS RUNS

Eichrom *LN* resins consist of porous polymer (Amberchrom CG71) particles of selected dimensions impregnated with HDEHP. The chemistry of the *LN* resin column run with feed/wash in 8 M HNO<sub>3</sub>–NaBrO<sub>3</sub> was the same in principle [1] as that of the BERKEX process; the only difference is the extractant—one was in solid resin form and the other in liquid organic form. The change from a one-stage SX process to a column separation has the advantages of a high number of plate stages for <sup>249</sup>Bk adsorption onto *LN* resins and a lack of organic liquid waste (HDEHP) disposal issues; however, operating parameters, such as the amount of <sup>249</sup>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.

Because both Bk(IV) and Ce(IV) were being adsorbed on *LN* resin (HDEHP), an attempt was made to selectively elute <sup>141,144</sup>Ce ahead of <sup>249</sup>Bk off the column by eluting the *LN* resin column with 0.15 M HNO<sub>3</sub> after Cf removal by 8 M HNO<sub>3</sub>–0.5 M NaBrO<sub>3</sub>, followed by <sup>249</sup>Bk stripping with other reagents.

The *LN* column elution profile is shown in Figure 5. The *LN* resin column (3 mL) run was performed in the following elution order: 9.2 BV of 8 M HNO<sub>3</sub>–0.5 M NaBrO<sub>3</sub>, including 1.7 BV (5.77 mL) of feed/washes; 6.4 BV of 0.15 M HNO<sub>3</sub>; 1 BV of 4 M HNO<sub>3</sub>; and 6.4 BV of 8 M HNO<sub>3</sub>. Co-adsorption of Bk and Ce with complete removal of Cf was as expected. Complete removal of Cf(III) and other divalent/trivalent impurities can be achieved within 6 BV of 8 M HNO<sub>3</sub>–0.5 M NaBrO<sub>3</sub>, including 1.7 BV of feed loading fraction. Both Bk and Ce were firmly retained on the resins after more than 10 BV of 8 M HNO<sub>3</sub>–0.5 M NaBrO<sub>3</sub> elution; therefore, the *LN* column worked as a “cut-off” column with no requirement of chromatographic control of effluent volume.



### 3 mL LN column:

Feed in 8 M  $\text{HNO}_3$ -0.5 M  $\text{NaBrO}_3$   
 Elution with 8 M  $\text{HNO}_3$ -0.5 M  $\text{NaBrO}_3$   
 Trial eluting Ce with 0.15 M  $\text{HNO}_3$  only  
 Trial eluting Ce with 4 M  $\text{HNO}_3$   
 Stripping with 8 M  $\text{HNO}_3$  No  $\text{H}_2\text{O}_2$

### Results:

**Complete separation of Cf** (not retained),  
 going with 8 M  $\text{HNO}_3$ -0.5 M  $\text{NaBrO}_3$   
**Bk and Ce retain**, follow-up separation of  
 Ce from Bk unsuccessful

Figure 5. The elution profile of LN (3.3 mL) resin column run.

To confirm complete removal of Cf(III) on the 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  $\text{HNO}_3$ -0.5 M  $\text{NaBrO}_3$ , including 6.8 BV (20.3 mL) of feed/washes, 2 BV of 0.15 M  $\text{HNO}_3$ , 2.1 BV of 4 M  $\text{HNO}_3$ , and 4 BV of 8 M  $\text{HNO}_3$ -0.45 M  $\text{H}_2\text{O}_2$  (Figure 6).

A larger volume of feed solution may occur when the Bk stripping fraction from an early column run is used directly, after addition of  $\text{NaBrO}_3$  but without volume reduction, to shorten the campaign process. The second LN column run with a 6.8 BV of feed/wash solution resulted in complete Cf removal within 8 BV of 8 M  $\text{HNO}_3$ -0.5 M  $\text{NaBrO}_3$  elution, even though the total elution of 8 M  $\text{HNO}_3$ -0.5 M  $\text{NaBrO}_3$  was in 11 BV.

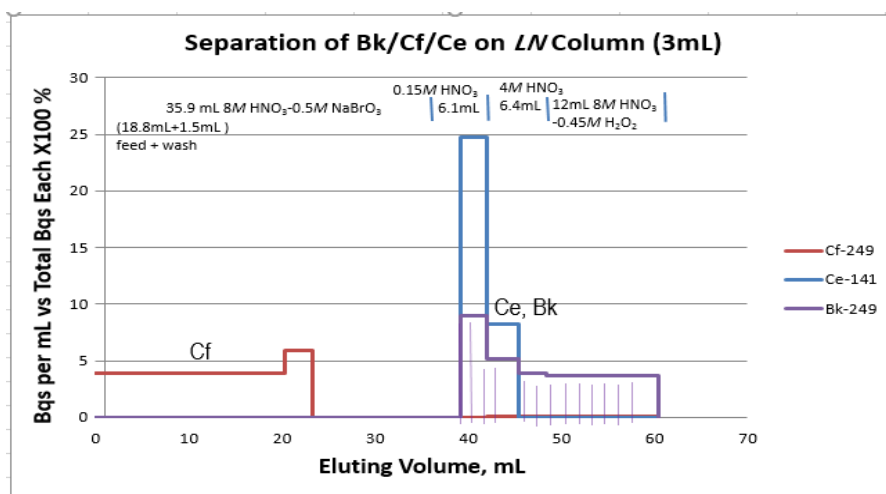


Figure 6. The elution profile of the second LN resin column (3 mL) run.

Two LN column runs demonstrated 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  $\text{HNO}_3$  was performed based on a study by Moore [2] for the purpose of selectively eluting  $^{141,144}\text{Ce}$  off the column ahead of the  $^{249}\text{Bk}$  stripping. Obviously, the selective stripping  $^{141,144}\text{Ce}$  by 0.15 M  $\text{HNO}_3$  was unsuccessful, with overlapping peaks of Ce and Bk in both LN column runs. In the first run, if the effluent were 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 the  $^{249}\text{Bk}$  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 the  $^{249}\text{Bk}$  product, which is clearly unacceptable for  $^{249}\text{Bk}$  production.

In Moore's work, an *LN* resin column (1.4 mL of L/D = 14) was used to separate trace amounts of  $^{249}\text{Bk}$  and  $^{144}\text{Ce}$ . Cerium-144 was completely removed with 7 BV of 0.15 *M*  $\text{HNO}_3$  elution without overlap and with a follow up  $^{249}\text{Bk}$  peak. Comparing Moore's study and experimental conditions with ours highlights at least three reasons for his success:

1. Moore used only tracer amounts of  $^{144}\text{Ce}$  and  $^{249}\text{Bk}$ . The Ce and Bk in our feed were 7 thousand and 4 million times greater, respectively, resulting in much greater peak widths for both  $^{144}\text{Ce}$  and  $^{249}\text{Bk}$  and a higher chance of peak overlap.
2. Moore used a feed of trivalent Bk(III) and Ce(III), whereas our selective eluting with 0.15 *M*  $\text{HNO}_3$  started with a transient process for reducing Bk(IV) and Ce(IV) 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, whereas our 0.15 *M*  $\text{HNO}_3$  elution started after more than 10 BV of 8 *M*  $\text{HNO}_3$ –0.5 *M*  $\text{NaBrO}_3$  elution in which both  $^{144}\text{Ce}$  and  $^{249}\text{Bk}$  had already migrated down into the column. Therefore, the case of the second *LN* resin column run with 12 BV of 8 *M*  $\text{HNO}_3$ –0.5 *M*  $\text{NaBrO}_3$  was even worse, in terms of Ce/Bk separation, than the first *LN* resin column run with 10 BV of 8 *M*  $\text{HNO}_3$ –0.5 *M*  $\text{NaBrO}_3$ .

Other journal studies have found that 0.15 *M*  $\text{HNO}_3$  may not be the optimal acidity for  $^{141,144}\text{Ce}$  to be selectively eluted off a column ahead of  $^{249}\text{Bk}$ . An ORNL report by Knauer and Weaver [3] indicates that the affinity of both  $^{249}\text{Bk}$  and  $^{144}\text{Ce}$  for HDEHP increases as the concentration of the eluting  $\text{HNO}_3$  decreases, but with a big difference. For example, at 1.0 *M*  $\text{HNO}_3$ , the  $K_d$  of Bk is 3 whereas that of Ce is only 0.03; at 0.15 *M*  $\text{HNO}_3$ , the  $K_d$  of Bk is 100 while that of Ce is unknown, but with a tendency toward a value higher than 1. Hence elution using  $\text{HNO}_3$  concentrations of >0.15 *M* but <1.0 *M* on a *LN* column may be the next candidate for separating Bk and Ce after Cf removal.

The open literature and our own experience show that  $\text{H}_2\text{O}_2$  in eluting  $\text{HNO}_3$  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 the half-filled  $5f^7$  or empty  $4f^0$  subshell, respectively.

### 3.2 BIORAD MP-1 RESIN COLUMN RUNS

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  $\text{H}_2\text{O}$  molecules as a result of the dipolar force of  $\text{H}_2\text{O}$  molecules and the charge density of ions). For cations ( $\text{M}^{n+}$ ) in high concentrations of an acid solution (HA),  $\text{H}_2\text{O}$  molecules of the inner sphere of the cation hydrate ions may be replaced by anions ( $\text{A}^-$ ) of the HA and thus form metal anions (e.g.,  $\text{MA}_m^{(m-n)-}$ ).

Actinides, particularly those with higher oxidation states, from Th to Bk, may form actinide anions in high concentrations of HCl or  $\text{HNO}_3$  and then be adsorbed on AX resins. The most familiar examples include Th(IV) in high  $\text{HNO}_3$  (but not in HCl), U (VI) in high HCl (but not in  $\text{HNO}_3$ ), and Pu(IV) in either high  $\text{HNO}_3$  or high HCl [4]. Berkelium (IV) has a smaller ionic size than the aforementioned tetravalent actinides (meaning a higher charge density), so the question is whether Bk(IV) will form anions to be adsorbed onto the AX resins.

An *MP-1* resin column (3.0 mL) run was performed in the following elution order: 10 BV of 8 *M*  $\text{HNO}_3$ –0.5 *M*  $\text{NaBrO}_3$ , including 2.3 BV of feed/washes; 8 BV of 8 *M*  $\text{HNO}_3$ ; and 4 BV of 8 *M*  $\text{HNO}_3$ –0.45 *M*  $\text{H}_2\text{O}_2$ . Figure 7 shows the elution profile and clearly indicates that the nitrate-complexed Ce(IV) anions

were adsorbed on *MP*-1 anion exchange resins, whereas the oxidized Bk(IV) was not adsorbed and was instead eluted out of the column together with trivalent Cf(III).

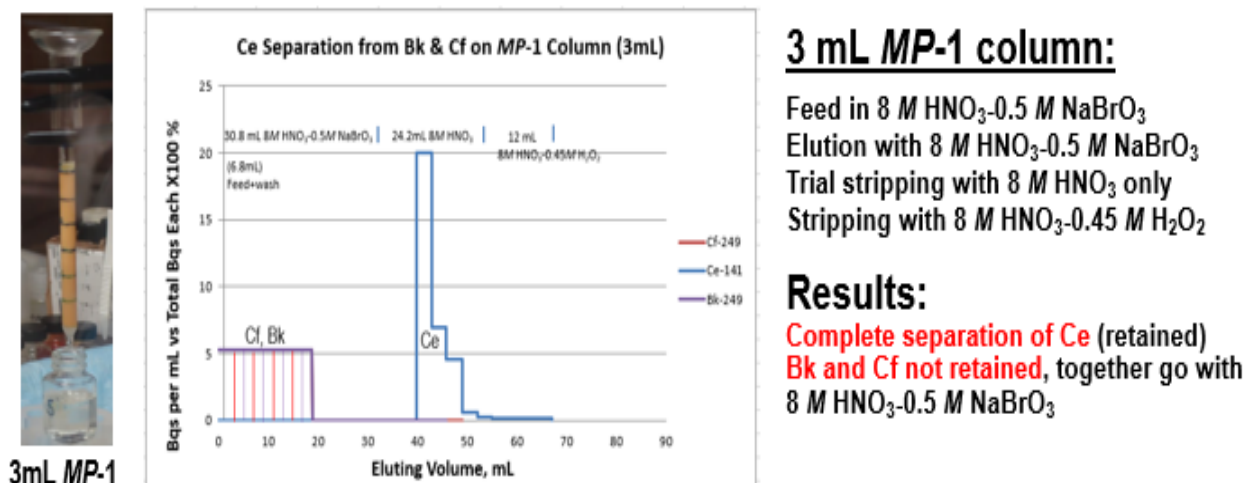


Figure 7. The elution profile of *MP*-1 resin column (3 mL) run.

Complete separation of Ce (retained) from Bk and Cf was achieved within 6.3 BV of 8 M HNO<sub>3</sub>-0.5 M NaBrO<sub>3</sub> elution, although 10.3 BV of 8 M HNO<sub>3</sub>-0.5 M NaBrO<sub>3</sub> elution was performed in this column run. Since the first 6.3 BV of effluent was collected into the same vial, it is not known whether the actual Bk/Cf peak ended before reaching 6.3 BV of 8 M HNO<sub>3</sub>-0.5 M NaBrO<sub>3</sub> elution. Even so, the Bk/Cf peak ended with 7 BV apart from the stripped Ce peak.

In this run, 8 M HNO<sub>3</sub> with no addition of H<sub>2</sub>O<sub>2</sub> was tested for stripping the adsorbed Ce(IV) off the column before a final stripping with 8 M HNO<sub>3</sub>-0.45 M H<sub>2</sub>O<sub>2</sub>. It took 6 BV of 8 M HNO<sub>3</sub> to strip the majority of the Ce off the column, which proves the necessity of using HNO<sub>3</sub>-H<sub>2</sub>O<sub>2</sub> to quickly strip Ce in future runs.

The most notable result for this *MP*-1 column run was that the oxidized Bk<sup>4+</sup> was not adsorbed by the AX *MP*-1 resin. The fact that <sup>249</sup>Bk(III) had been oxidized to tetravalent state in this *MP*-1 column run was confirmed because Ce(III) of similar *E*<sup>0</sup> (see Table 1) had been oxidized and adsorbed on the *MP*-1 resin. Also, in the same 8M HNO<sub>3</sub>-0.5M NaBrO<sub>3</sub> solution used in all of the 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 for the reason why Bk<sup>4+</sup> was not, as Ce<sup>4+</sup> does, adsorbed by the *MP*-1 resin is that the oxidized Bk(IV) did not, as Ce<sup>4+</sup> does, form anion complexes in 8M HNO<sub>3</sub> and thus was not adsorbed by AX *MP*-1 resin.

In a review of previous experiments at REDC, instances of oxidized Bk ions not being adsorbed on *MP*-1 resin were encountered; however, the cause was thought to be oxidation failure due to improper oxidation conditions. The presence of Ce in recent experiments helped to clarify those previous observations. Further literature studies indicated that early in 1976, F. L Moore, an ORNL chemist, found this “surprising sorption behavior difference of Bk(IV) and Ce(IV) nitrate anions on AX resins” [5] and tried to explain it as the weaker formation of Bk(IV) nitrate anions due to the smaller ionic radius of Bk(IV) ions (0.86 Å) compared with Ce(IV) ions (0.92 Å); i.e. both Bk(IV) and Ce(IV) form nitrate anions, but their resulting sorption ability on AX resins is different. Since then, no complexation constant values have been reported for Bk(IV), but one study by Makarova et al. [6] explored possible reasons for this Bk(IV) behavior via comparative electromigration. Electromigration of Bk(IV) and Ce(IV) in mixed HNO<sub>3</sub>-HClO<sub>4</sub> solutions at *I* = 6 M, and of Bk(IV), Pu(IV), Th(IV), Ce(IV) in the HNO<sub>3</sub> range of 2~16 M,

showed that Bk(IV) in 3~6 *M* HNO<sub>3</sub> migrated as monovalent cations, e.g., [Bk(H<sub>2</sub>O)<sub>x</sub>(NO<sub>3</sub>)<sub>3</sub>]<sup>+</sup>, but behaved as negatively charged ions only at ≥10*M* HNO<sub>3</sub>. The Makarova study explained why Bk(IV) did not adsorb on the *MP*-1 resins in 8 *M* HNO<sub>3</sub>–NaBrO<sub>3</sub>. It also suggested the possible formation of nitrate-complexed Bk(IV) anions in ≥10 *M* HNO<sub>3</sub> media.

**Table 1. Standard reduction potentials (*E*<sup>o</sup>) of concerned ions.**

Half-reactions	<i>E</i> <sup>o</sup> (V)
$\text{O}_2(\text{g}) + 2 \text{H}^+_{(\text{aq})} + 2\text{e}^- \rightleftharpoons \text{H}_2\text{O}_{2(\text{aq})}$	+0.68
$\text{Br}_2(\text{l}) + 2\text{e}^- \rightleftharpoons 2 \text{Br}^-_{(\text{aq})}$	+1.07
$\text{Cr}_2\text{O}_7^{2-}_{(\text{aq})} + 14 \text{H}^+_{(\text{aq})} + 6\text{e}^- \rightleftharpoons 2 \text{Cr}^{3+}_{(\text{aq})} + 7 \text{H}_2\text{O}$	+1.33
$\text{Cl}_2(\text{l}) + 2\text{e}^- \rightleftharpoons 2 \text{Cl}^-_{(\text{aq})}$	+1.36
$\text{BrO}_3^- + 6 \text{H}^+_{(\text{aq})} + 6\text{e}^- \rightleftharpoons \text{Br}^-_{(\text{aq})} + 3 \text{H}_2\text{O}$	+1.44
$\text{Ce}^{4+}_{(\text{aq})} + \text{e}^- \rightleftharpoons \text{Ce}^{3+}_{(\text{aq})}$	+1.61
$\text{Bk}^{4+}_{(\text{aq})} + \text{e}^- \rightleftharpoons \text{Bk}^{3+}_{(\text{aq})}$	+1.67
$\text{H}_2\text{O}_2(\text{aq}) + 2 \text{H}^+_{(\text{aq})} + 2\text{e}^- \rightleftharpoons 2 \text{H}_2\text{O}$	+1.77

The fact that only Ce(IV) adsorbed on the *MP*-1 AX column and Bk(IV) did not was encouraging, rather than discouraging, because the removal of <sup>141,144</sup>Ce from <sup>249</sup>Bk by the *MP*-1 resin column appeared more efficient and complete than the originally planned processing route: Cf removal on an *LN* resin column followed by selective elution of Ce off the column before Bk. The different adsorption features of the *MP*-1 and *LN* resins inspired a new processing route for purification of <sup>249</sup>Bk in the Bk Finishing step of the processing campaign.

### 3.3 DUAL COLUMN ARRANGEMENT FOR SEPARATING Bk FROM Cf AND Ce

In an 8 *M* HNO<sub>3</sub>–0.5 *M* NaBrO<sub>3</sub> media, the *MP*-1 resin column adsorbs Ce(IV) selectively, allowing Bk(IV) and Cf(III) to pass through the column, whereas 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 enabled the design of a new dual-column arrangement for separating <sup>249</sup>Bk from Cf, Ce and non-rad impurities as follows:

1. Prepare one *MP*-1 resin column and one *LN* resin column and condition both with an 8 *M* HNO<sub>3</sub>–0.5 *M* NaBrO<sub>3</sub> solution. Prepare the feed (Bk, Cf, Ce, and non-rad impurities) in a minimum volume of 8 *M* HNO<sub>3</sub>–0.5 *M* NaBrO<sub>3</sub> solution, as well the 8 *M* HNO<sub>3</sub>–0.5 *M* NaBrO<sub>3</sub> solution, before the column run.
2. Pass the feed/washes (both in 8 *M* HNO<sub>3</sub>–0.5 *M* NaBrO<sub>3</sub>) and 4 BV of 8 *M* HNO<sub>3</sub>–0.5 *M* NaBrO<sub>3</sub> through the *MP*-1 resin column to adsorb <sup>141,144</sup>Ce selectively, and allow the *MP*-1 effluent (Bk, Cf, and non-rad impurities) to immediately enter the *LN* resin column to adsorb <sup>249</sup>Bk.
3. Put the *MP*-1 resin column (with Ce) aside for later treatment. The <sup>141,144</sup>Ce on the *MP*-1 resin column can either simply be disposed of with the column as solid waste or be stripped off the column with 0.15 *M* HNO<sub>3</sub>–0.45 *M* H<sub>2</sub>O<sub>2</sub> if the *MP*-1 column is to be reused.









### 3.4 DISCUSSIONS

#### 3.4.1 Possibilities of Using Dual-Column Method in Processing Campaign Ahead of Bk Finishing

The dual-column method extracts Bk(IV) by itself, and the column scale can easily be 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  $^{249}\text{Bk}$  is extracted, the higher the  $^{249}\text{Bk}$  production will be in terms of reduced decay loss.

In the current post-irradiation processing campaign (see Figure 2), the following options exist for using the dual-column method:

1. Immediately after nitric acid dissolution of the irradiated target before the CLEANEX process, with the  $\text{HNO}_3$  solution containing dissolved trans-plutonium elements and all impurities including Ln
2. Immediately after the CLEANEX process, before the two LiCl AX processes, with the  $\text{HNO}_3$  (Instead of the current HCl) solution containing all dissolved trans-plutonium elements and Ln FP impurities
3. Immediately after LiOH precipitation for  $\text{Cl}^-$  removal before the hot cell operation of CX with AHIB, with the  $\text{HNO}_3$  solution containing trans-Cm elements (no Cm and Am) and only 1% of FP impurities
4. Immediately after the two LiCl AX processes, before LiOH precipitation, with a HCl (not  $\text{HNO}_3$ ) solution to be treated containing the same element content as in possibility 3, but in a HCl media

For **Option 1**, the composition of the  $\text{HNO}_3$  solution to be treated is much more complicated than that in Bk Finishing. The tetravalent elements present in solution include  $\text{Bk}^{4+}$ ,  $\text{Ce}^{4+}$ ,  $\text{Pu}^{4+}$ ,  $\text{Zr}^{4+}$  or more, but the latter three should all be adsorbed on the MP-1 resin “filter” with only  $\text{Bk}^{4+}$  being selectively adsorbed on the LN resin column. LN resin shouldn’t retain Ln FPs in 8M  $\text{HNO}_3$  ( $K_d < 10$ ) so the feed for the later CLEANEX process with the 8 M  $\text{HNO}_3$ –0.5 M  $\text{NaBrO}_3$  solution (without Bk, Ce) should be no more difficult to prepare than the solution from Nitric Acid Dissolution, as long as the  $\text{BrO}_3^-$  is removed by pre-heating (see Figure 11).

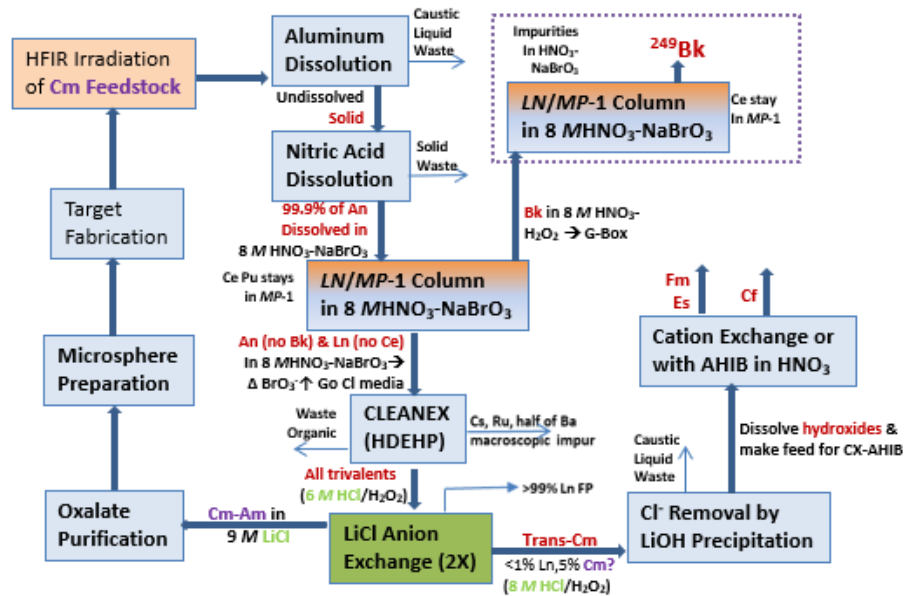
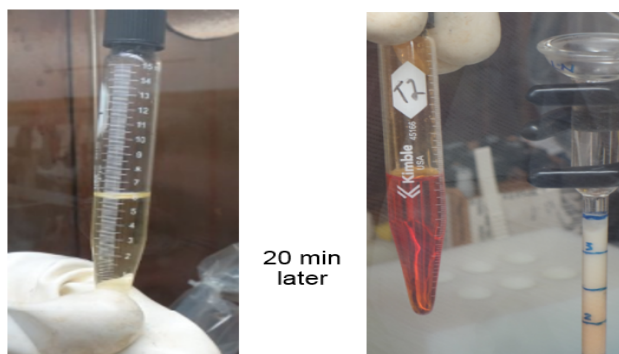


Figure 11. The post-irradiation processing with implementing the dual column after acid dissolution.

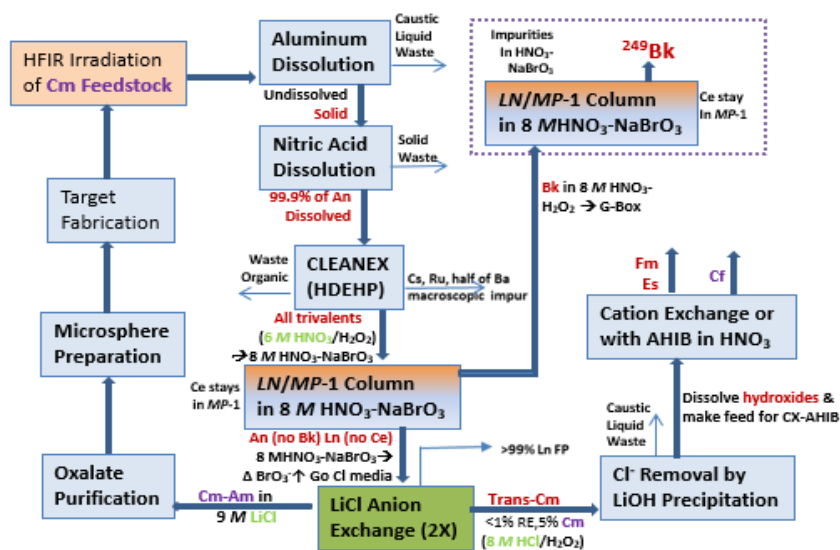
The issues for this option concern the radiation resistance of the *LN* and *MP-1* resins and  $\text{BrO}_3^-$ , the oxidizer used for  $\text{Bk}^{3+} \rightarrow \text{Bk}^{4+}$ , because the radiation dose of the dissolved target would be millions of times higher than in the Bk Finishing process. Radiation-induced reduction of  $\text{NaBrO}_3$  to  $\text{Br}^-$  or  $\text{Br}_2$  (the solution turns orange) has already been observed in Bk Finishing and it is the reason for requiring that the solution be used within 20~30 minutes after mixing with the radioactive solution (see Figure 12). Certainly, the situation of  $\text{NaBrO}_3$  reduction would be worse if  $\text{NaBrO}_3$  were directly introduced into the dissolved target solution with a radiation dose millions of times higher.



**Figure 12. Radiation-induced reduction of  $\text{BrO}_3^-$  after mixing with radionuclides.**

The compound  $\text{CrO}_3$  should be a good substitute for  $\text{NaBrO}_3^-$  (see Table 1) as an oxidizer with higher radiation resistance that has been used safely in the BERKEX process in previous years. It would need to be tested if used directly with a dissolved target solution.

For **Option 2**, the stream of trivalent elements from CLEANEX has been separated from high gamma emitters of  $^{137}\text{Cs}$ ,  $^{103}\text{Ru}$  and half of  $^{140}\text{Ba}$ , so the dose of feed for the dual-column run is reduced.



**Figure 13. Post-irradiation processing implementing the dual column method after the CLEANEX process.**

The stream of trivalent elements from CLEANEX can be either in 6 M  $\text{HNO}_3$  or 6 M  $\text{HCl}$ , while the dual column process requires a feed in  $\text{HNO}_3\text{-NaBrO}_3$  (not  $\text{HCl}$ ). The follow-up  $\text{LiCl}$  process requires a feed in  $\text{HCl}$  from the 8 M  $\text{HNO}_3\text{-0.5 M NaBrO}_3$  stream of the dual column process, which adds more operations

of a conversion of  $\text{HNO}_3\text{-NaBrO}_3$  into a  $\text{HCl}$ , e.g. drying down for  $\text{BrO}_3^-$  removal and  $\text{HNO}_3$  media change (see Figure 13).

For **Option 3**, it is easier to adjust the solution from  $\text{LiOH}$  precipitation into the feed for the dual column process than into the feed for the original CX with AHIB process (Option 3 eliminates the step of adjusting acidity from high  $\text{HNO}_3$  to low  $\text{HNO}_3$  with AHIB). However, the 8 M  $\text{HNO}_3\text{-}0.5\text{ M NaBrO}_3$  solution (trans-Cm elements but no Bk) from the dual column process needs to be dried for  $\text{BrO}_3^-$  removal and  $\text{HNO}_3$  acidity adjustment for the subsequent CX with AHIB. In possibility 3, the solution to be treated by the dual column process has a much lower radiation dose, since 99.9% of lanthanide FPs and Am-Cm are removed in previous processing steps (see Figure 14).

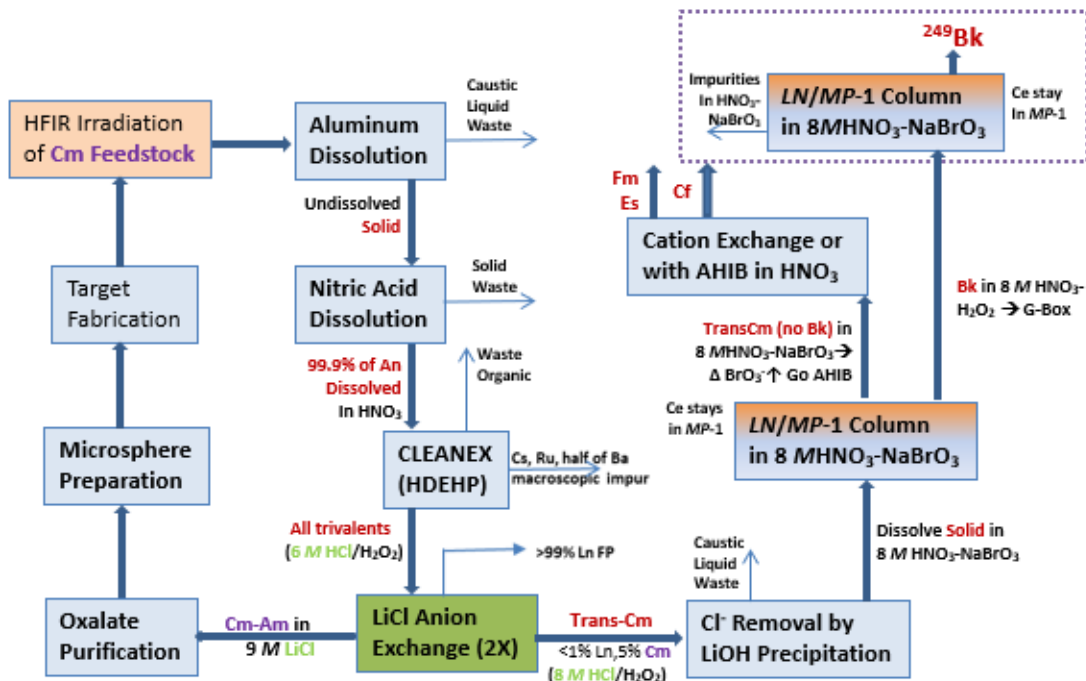


Figure 14. Post-irradiation processing implementing the dual column method after  $\text{LiOH}$  precipitation.

For **Option 4**, the dose and composition of the solution to be treated by the dual column process will be similar to possibility 3; the biggest difference is that the solution is in  $\text{HCl}$  media (see Figure 15). The issue is whether the dual column process will be able to use a feed of  $\text{HCl}$ -oxidizer.

Table 1 shows that  $\text{BrO}_3^-$  will not work as a proper oxidizer in  $\text{HCl}$  because it will first oxidize  $\text{Cl}^-$  instead of oxidizing  $\text{Bk}^{3+}$ . One unsuccessful  $\text{MP-1}$  resin column run was performed with  $^{249}\text{Bk}$  in 8 M  $\text{HCl}\text{-}0.5\text{ M NaBrO}_3$ , for the purpose of determining whether  $\text{Bk}^{4+}$  would be adsorbed on an anion exchange resin or not. Concerns regarding whether  $\text{BrO}_3^-$  would be reduced by  $\text{Cl}^-$  triggered a pre-test that involved titrating 2 M  $\text{NaBrO}_3$  into 12 M  $\text{HCl}$  (with no Bk) then adding  $\text{MP-1}$  resin into the cell to observe the color change and vapor generation. The concentrations of  $[\text{BrO}_3^-]$  in the cell increased to 0.67 M with  $[\text{HCl}]$  decreasing from 12 M to 8 M. Solution color changes were observed upon the addition of  $\text{NaBrO}_3$  (see Figure 16) and a smell of  $\text{Cl}_2$  was observed during titration. Although the color change implied that  $\text{BrO}_3^-$  was reducing to  $\text{Br}^-$ , the  $\text{MP-1}$  resin column run was performed later with  $^{249}\text{Bk}$  and  $^{141,144}\text{Ce}$ , since the pre-test showed no obvious bubble-disturbance in the resin bed for a column run.

The results for this *MP-1* resin column run showed both  $^{249}\text{Bk}$  and  $^{141,144}\text{Ce}$  were not adsorbed on the resin because of the obvious consumption of  $\text{BrO}_3^-$  by  $\text{HCl}$ . The bright yellow band of  $\text{Br}^-$  on the *MP-1* resin indicated the extent of  $\text{BrO}_3^-$  reduction (Figure 16).

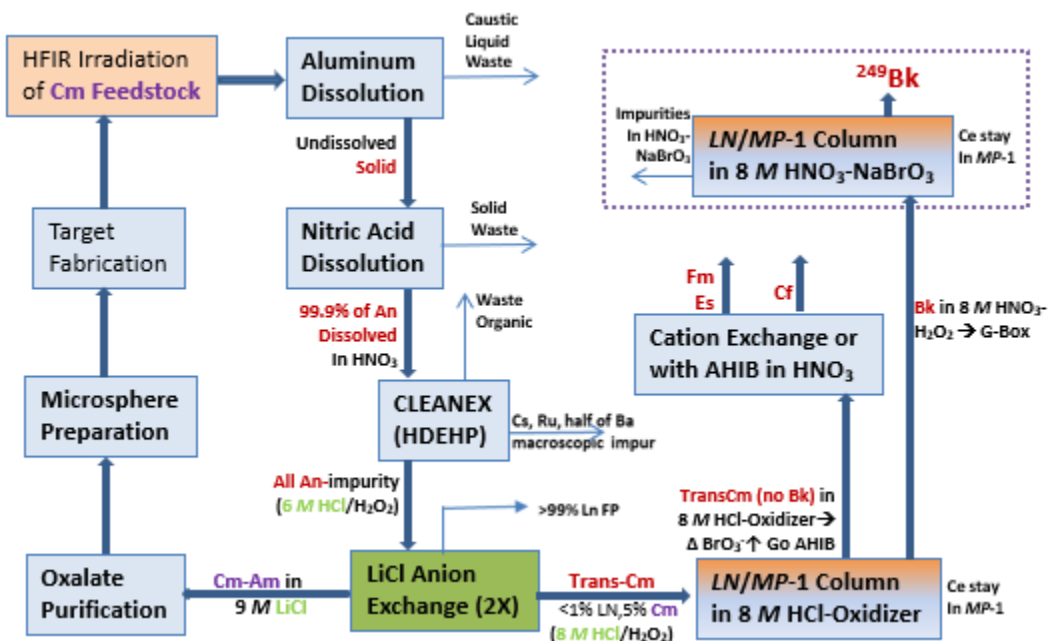


Figure 15. Post-irradiation processing implementing the dual column method after LiCl AX processing.

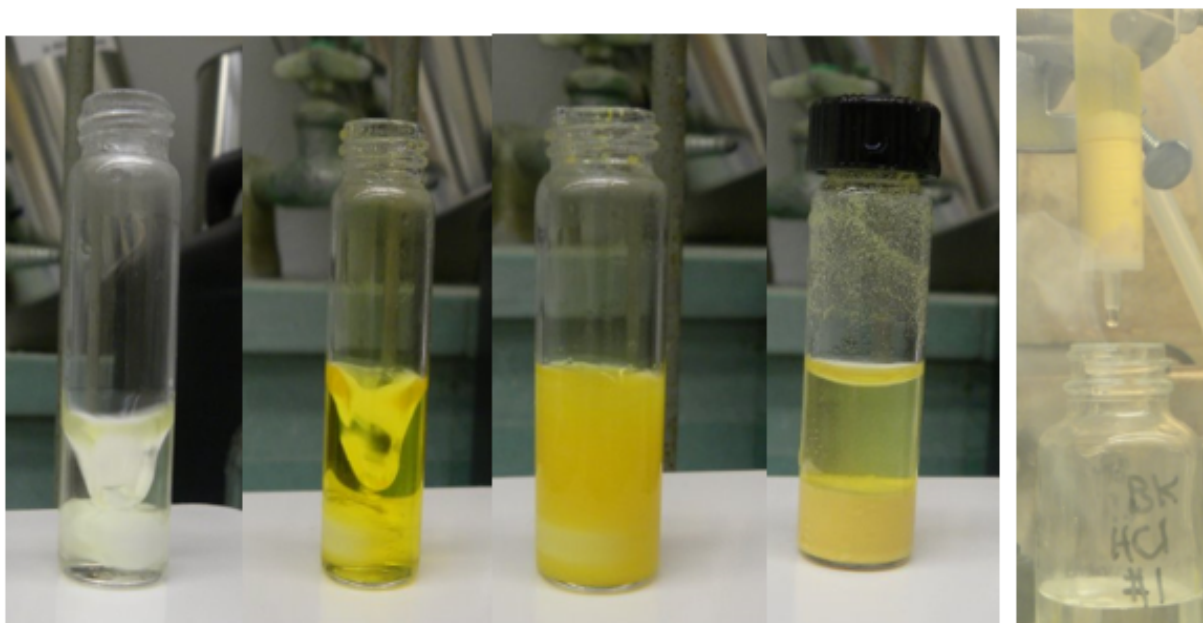


Figure 16. (Left)  $\text{HCl}$ ; (second from left)  $\text{NaBrO}_3$  added; (third from left) *MP-1* resin added; (fourth from left) resin settled. (Right) an *MP-1* column run with  $^{249}\text{Bk}$  in  $8\text{ M HCl}$ - $\text{NaBrO}_3$ .

Many other oxidizers were successfully used in previous Bk production, e.g.  $\text{CrO}_3$  ( $\text{Cr}_2\text{O}_7^{2-}$ ),  $\text{O}_3$ , and  $\text{AgO}$ . However,  $\text{Cr}_2\text{O}_7^{2-}$  is probably the best candidate for future work, since its use at the REDC in previous high-acidity trials has shown no reduction by  $\text{HCl}$  (Table 1).

The exploration of the four possible processing routes to using the dual-column method before current Bk Finishing indicates that the potential of further shortening the extraction and purification of  $^{249}\text{Bk}$  does exist. However, there is a need for additional confirmative experiments, e.g., tests of the radiation resistance of other oxidizers than  $\text{BrO}_3^-$  for  $\text{Bk(III} \rightarrow \text{IV)}$  and trials of the use of an 8 M  $\text{HCl}$ –oxidizer in dual column runs, followed by elution/stripping with  $\text{HNO}_3$  media.

The major uncertainty with regard to using the dual column method in the possible campaign processing alternatives that were discussed is the possibility of radiation damage to the oxidizer  $\text{BrO}_3^-$  due to the large amounts of total actinides in the process. But the dual column method can be used for  $^{249}\text{Bk}$  analysis of the samples from any step of the Cf campaign, so long as the sample size is controlled within 1 mg of the total actinides. An operational procedure for  $^{249}\text{Bk}$  analysis of a sample from the processing campaigns is described in Appendix A.

The more revolutionary production route for  $^{249}\text{Bk}$  would be a  $^{249}\text{Bk}$ -specific production campaign using enriched  $^{248}\text{Cm}$  (not a 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  $^{249}\text{Bk}$  burnup in hopes of tripling the  $^{249}\text{Bk}$  yield at the reactor discharge. The dual-column method will be used directly on the dissolved target material for  $^{249}\text{Bk}$  extraction and purification in a much shorter post-irradiation processing campaign.

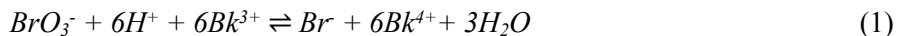
Two topics of concern of Bk chemistry are discussed in the following paragraphs.

### 3.4.2 Redox Issues of Concerned Radionuclides and Reagents

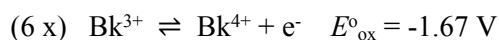
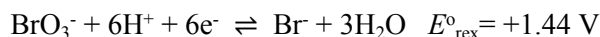
**Table 1** gives  $E^\circ$  values of relevant half-cell reactions and follows the simple rule: from top to bottom, the more positive the potential, the easier (of the reactant in half cell) to be reduced; or from bottom to top, the more negative the potential, the easier (of the reactant in half cell) to be oxidized.

By that we notice that  $\text{BrO}_3^-$  seems unable to oxidize  $\text{Bk(III)}$  to  $\text{Bk(IV)}$ . Calculation of the cell potential,  $E_{\text{cell}}$ , of the presumed redox reaction will result in a cell potential value. Only a positive cell potential value shows the driving force for the presumed reaction, while a negative cell potential value no driving force to the presumed reaction. Let us first calculate  $E_{\text{cell}}^\circ$ , the cell potential at standard state of the reaction Eq. (1) and then calculate  $E_{\text{cell}}$ , the cell potential at non-standard state of the Eq. (1):

The balanced reaction of oxidation of  $\text{Bk(III)}$  to  $\text{Bk(IV)}$  by  $\text{BrO}_3^-$  can be expressed as:



The half reactions of Eq. (1) are:



The cell potential  $E_{\text{cell}}^\circ$  of Eq. (1) **at standard state** (concentrations of 1 mol/L at 25°C) is calculated as:

$$E_{\text{cell}}^\circ = E_{\text{red}}^\circ + E_{\text{ox}}^\circ = 1.44 + (-1.67) = -0.23 \text{ (V)} \quad (2)$$

The negative result of  $E^\circ_{\text{cell}}$  shows unfavorable to the Eq. (1) at standard state.

In reality, Eq. (1) is at **non-standard state**, so let us calculate the cell potential at non-standard state of the Eq. (1) based on the Nernst Equation (3) as:

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{RT}{nF} \ln Q = E^\circ_{\text{cell}} - \frac{8.314 \times 313}{6 \times 96485} 2.30258 \log Q = E^\circ_{\text{cell}} - 0.01035 \log Q \quad (3)$$

Where

$n$  is the number of moles of electrons transferred in the balanced Eq. (1), which is equal to **6**,  
 $F$  is the Faraday constant (96,485 C/mol),  
 $T$  is the Eq. (1) temperature in kelvin, = 313°K (**40°C inside hot cell**),  
 $R$  is the universal gas constant, = 8.314 J/ (K. mol)

$$\text{The reaction Eq.(1) quotient } Q = \frac{[\text{Products}]}{[\text{Reactants}]} = \frac{[\text{Br}^-][\text{M}^{4+}]^6 a_{\text{H}_2\text{O}}^3}{[\text{BrO}_3^-][\text{H}^+]^6 [\text{M}^{3+}]^6} \quad (4)$$

With the calculated value of  $E^\circ_{\text{cell}} = -0.23$  V, the equation (3) can be simplified as:

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{RT}{nF} \ln Q = -0.23 - 0.01035 \log Q \quad (5)$$

It is known that **only a positive  $E_{\text{cell}}$  to make the combined reaction Eq. (1) work**. To have a positive cell potential (i.e.  $E_{\text{cell}} > 0$ ), 0.01035 log Q must be mathematically less than -0.23, i.e.

$$0.01035 \log Q < -0.23 \quad \text{or} \quad \log Q < -22.222 \quad \text{or} \quad Q < 10^{-22.222} \text{ (towards zero)} \quad (6)$$

The reality is that the **Q value of Eq. (1) will definitely be larger than 1** with following concentrations into Eq. (4):

$[\text{BrO}_3^-]_{\text{initial}} = 0.5$  M (supposing 10% converts to  $\text{Br}^-$  by the end of the reaction);  
 >99% of  $\text{Bk}^{3+}$  is oxidized to  $\text{Bk}^{4+}$  at the end of reaction;  $[\text{H}^+]_{\text{initial}} = 8$  M;  
 $a_{\text{H}_2\text{O}}$  (in 8M  $\text{HNO}_3$ ) is < 1 (approach 1, if in very dilute solution).

What caused the confliction of calculations vs. reality?

A better explanation would be that **the real potential  $E^\circ$  for ( $\text{Bk}^{4+}/\text{Bk}^{3+}$ ) couple must be more negative than the published  $E^\circ = 1.67\text{V}$** , due to the existence of the high complexing agent HDEHP ( $LN$  resins).

We knew that the published  $E^\circ = 1.67\text{V}$  was averaged from many measured results in media of low complexing capability (mostly in perchlorate solution, where  $\text{ClO}_4^-$  complexing capability approaching zero). The history of  $E^\circ$  measurements for the ( $\text{Bk}^{4+}/\text{Bk}^{3+}$ ) couple shows the results of 1.36V in sulfuric acid and 1.12V in phosphoric acid. It would be reasonable to say that the potential  $E^\circ$  for the ( $\text{Bk}^{4+}/\text{Bk}^{3+}$ ) couple must be more negative than 1.44V ( $E^\circ$  value for the couple of  $\text{BrO}_3^-/\text{Br}^-$ ) in our working conditions with a strong complexing agent HDEHP ( $LN$  resins), which have higher complexing capability than sulfuric or phosphoric acids. It should be more negative than 1.33V ( $E^\circ$  value for the couple of  $\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}$ ), since the chromate was also successfully used for  $\text{Bk}(\text{III} \rightarrow \text{IV})$  oxidation in previous  $^{249}\text{Bk}$  campaign with HDEHP solvent extraction.

Table 2 shows some historically measured potentials of  $\text{Bk}(\text{IV})/\text{Bk}(\text{III})$  under various conditions, selected from the Table 10.4, page 1481 of the chapter “Berkelium” by Hobart and Peterson in reference [7].



Among these data,  $E^0$  values changes from 1.43V to 1.36V with increase of  $[\text{H}_2\text{SO}_4]$  from 0.1  $M$  to 2  $M$  when measured by same method of direct potentiometry.

**Table 2. Measured potentials of Bk(IV) / Bk(III) couples in the literature.**

(V vs. NHE)	Conditions <sup>a</sup>	References
1.6 ± 0.2	Calc.	Nugent et al. (1973,1976)
1.664	Calc.	Simakin et al. (1977)
1.54 ± 0.1	1 $M$ $\text{HClO}_4$ , dir. pot	Stokely et al. (1972)
1.597 ± 0.005	1 $M$ $\text{HClO}_4$ , dir. pot	Simakin et al. (1977)
1.595 ± 0.005	1 $M$ $\text{HClO}_4$ , spectroelectro	Antonio et al. (2002)
1.735 ± 0.005	9 $M$ $\text{HClO}_4$ , dir. pot	Simakin et al. (1977)
1.54 ± 0.1	1 $M$ $\text{HNO}_3$ , dir. pot	Stokely et al. (1972)
1.562 ± 0.005	1 $M$ $\text{HNO}_3$ , dir. pot	Simakin et al. (1977)
1.56	6 $M$ $\text{HNO}_3$ , SX	Musikas et al. (1967)
1.6	3-8 $M$ $\text{HNO}_3$ , coprecip	Thompson et al. (1950)
1.543 ± 0.005	8 $M$ $\text{HNO}_3$ , dir. pot	Simakin et al. (1977)
1.43	0.1 $M$ $\text{H}_2\text{SO}_4$ , dir.pot	Propst et al. (1970)
1.44	0.25 $M$ $\text{H}_2\text{SO}_4$ , SX	Musikas et al. (1967)
1.38	0.5 $M$ $\text{H}_2\text{SO}_4$ , dir.pot	Stokely et al. (1969)
1.42	0.5 $M$ $\text{H}_2\text{SO}_4$ , SX	Musikas et al. (1967)
1.37	1 $M$ $\text{H}_2\text{SO}_4$ , dir.pot	Stokely et al. (1969)
		Kulyako et al. (1981)
1.36	2 $M$ $\text{H}_2\text{SO}_4$ , dir.pot	Stokely et al. (1969)
		Kulyako et al. (1981)
1.12 ± 0.1	7.5 $M$ $\text{H}_3\text{PO}_4$ , dir.pot	Stokely et al. (1972)
0.85	0.006 $M$ $\text{K}_{10}\text{P}_2\text{W}_{17}\text{O}_{61}$ ,	Baranov et al. (1981)

<sup>a</sup>Calc. = calculated value; dir.pot = direct potentiometry; SX = solvent extraction, spectroelectro = spectroelectrochemistry; coprecip = coprecipitation.

### 3.4.3 Possibility of Complexed Bk(IV) Anion Formation

The purpose of investigating the possibility of actinide anion formation is to use this feature in the separation of actinides in high  $\text{HNO}_3$  and  $\text{HCl}$ , which are most commonly used in actinide chemistry. The possibility of complexed anion formation for individual tetravalent actinides is known to be influenced by many factors, including the following.

**Charge density.** Generally speaking, the higher the charge density of a metal ion, the higher the possibility for it to complex with  $\text{NO}_3^-$  or  $\text{Cl}^-$  in high  $\text{HNO}_3$  or  $\text{HCl}$  so as to form a metal anion. The charge densities of actinides of the same tetravalent state are decided by their ion sizes.

The third row of Table 3 shows the ionic radii of tetravalent actinides changing with atomic numbers, showing a trend of decreasing ionic radius that implies an increasing charge density along the row. But the possibility of forming complexed actinide anions in high  $\text{HNO}_3$  or  $\text{HCl}$ , summarized on the fifth and



sixth row of the table, does not follow the same trend of charge density because of other influencing factors.

**Table 3. Features influencing the formation of actinide anions.**

<b>An<sup>4+</sup></b>		<b>Th<sup>4+</sup></b>	<b>Pa<sup>4+</sup></b>	<b>U<sup>4+</sup></b>	<b>Np<sup>4+</sup></b>	<b>Pu<sup>4+</sup></b>	<b>Am<sup>4+</sup></b>	<b>Cm<sup>4+</sup></b>	<b>Bk<sup>4+</sup></b>	<b>Cf<sup>4+</sup></b>	<b>Es<sup>4+</sup></b>
Atomic No.		90	91	92	93	94	95	96	97	98	99
Ionic radii, Å <sup>e</sup>		0.94	0.90	0.89	0.87	0.86	0.85	0.85	0.83	0.82	/
Electronic configuration	[Rn]7s <sup>0</sup> 6d <sup>0</sup>	5f <sup>0</sup>	5f <sup>1</sup>	5f <sup>2</sup>	5f <sup>3</sup>	5f <sup>4</sup>	5f <sup>5</sup>	5f <sup>6</sup>	5f <sup>7</sup>	5f <sup>8</sup>	5f <sup>9</sup>
Formation of anions?	High HNO <sub>3</sub>	Yes 8M	Yes / <sup>a</sup>	Yes Yes <sup>c</sup>	Yes >6M	Yes >4M	No	No	Yes >10M	No	No
	High HCl	No	Yes Yes <sup>b</sup>	Yes Yes <sup>d</sup>	Yes >8M	Yes >8M	No	No	??	No	No

a. Pa(V) has  $K_d=50$  at 8M HNO<sub>3</sub>, not with Pa(IV).

b. Yes, only with Pa (V) at >6 M HCl.

c. In HNO<sub>3</sub>, U(IV)  $K_d=100$  at 4 M, U(VI)  $K_d=16$  at 8 M.

d. In HCl, anions of U(VI) at >6 M, and of U(IV)  $K_d>100$  at  $\geq 10$  M.

e. Shannon, R. D. (1976) Acta Crystallogr. A, 32, 751-67

**Stability of actinides in tetravalent states.** Obviously, instable tetravalent actinides An<sup>4+</sup> have no chance to form complexed anions. Both actinides (5f) and lanthanides (4f) are *f*-block elements, but the former has larger atomic and ionic radii than the latter, are prone to hybridization, and exhibit a larger variety of valence states. The lighter actinides (Th to Pu) with fewer *f* electrons show much more variable valence because of the similarity of the electron energies in the 5f, 7s, and 6d shells. Among the lighter actinides, only Th<sup>4+</sup> and Pu<sup>4+</sup> are in their most stable valence states; the other three are in an order of stability Np<sup>4+</sup> > U<sup>4+</sup> > Pa<sup>4+</sup>. Tetravalent Pa(IV) easily oxidizes to its most stable pentavalent state Pa(V) by losing its 5f<sup>1</sup> electron in solution, while U<sup>4+</sup> is stable in absence of air but is oxidized by oxygen. In  $\geq 8M$  HNO<sub>3</sub> and HCl used in our experiments, hexavalent UO<sub>2</sub><sup>2+</sup> is in the most stable state. Neither U(IV) nor U(VI) in HNO<sub>3</sub> form strong anions, but U(VI) in HCl forms stable anions, e.g., UO<sub>2</sub>(Cl<sub>4</sub>)<sup>2-</sup>, with only weak anions of U(IV) at  $\geq 10$  M HCl.

The heavier actinides (from Am onward) with more 5f electrons behave similarly to the lanthanides; they show stable trivalent states only in acids, with Bk<sup>4+</sup> as the only exception (the solution conditions when higher valences of Am(IV-VII) and Cm(IV) formed were either basic or in electrolytic cells).

As mentioned earlier, Bk(IV) shows reasonable stability in solution in the absence of reducing agents because of the stabilizing influence of its half-filled 5f<sup>7</sup> subshell. All experiment results told us that no anions are formed for Bk<sup>4+</sup> in HNO<sub>3</sub> up to 10 M, with one experiment implying that at  $\geq 10$  M HNO<sub>3</sub>, anions of Bk(IV) are likely formed. What about the possibility of complexed Bk(IV) anion formation in high HCl? With less geometric hindrance, will the Cl<sup>-</sup> ions enter the inner spheres of Bk<sup>4+</sup> ions more easily than NO<sub>3</sub><sup>-</sup> ions to form Bk(IV) anions in high HCl media?

This discussion is not simply academic curiosity, but a feature of the study of Bk that is potentially important for future Bk separation and purification.

#### 4. CONCLUSION

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

To satisfy the increasing demand for  $^{249}\text{Bk}$ , a campaign is needed specifically aimed at the production of  $^{249}\text{Bk}$  using enriched  $^{248}\text{Cm}$  as an irradiation target and the thermal neutron filter technique to reduce  $^{249}\text{Bk}$  burnup during target irradiation. The lower yield of FP impurities and less complicated target components of the campaign would allow use of the dual-column method for direct separation of  $^{249}\text{Bk}$  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  $^{249}\text{Bk}$  can be used in the early steps of the current multi-step processing campaign. Further studies of Bk redox chemistry and tetravalent  $\text{Bk}^{4+}$  anion formation would be beneficial to  $^{249}\text{Bk}$  production in a long run.

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## APPENDIX A. Bk-249 ANALYSIS FOR SAMPLES FROM THE CF CAMPAIGN PROCESS

**The Underlying Principle of the Dual Column Method** for selective separation of  $^{249}\text{Bk}$  from all other actinides and impurities

- **LN resin** retains ONLY Bk(IV)(If without impurities of  $^{141,144}\text{Ce}$ ) in  $8M \text{HNO}_3$ – $0.5M \text{NaBrO}_3$  and Bk(IV) is desorbed from LN resin with  $\text{HNO}_3$ – $\text{H}_2\text{O}_2$  elution.
- **MP-1 resin** retains Ce(IV) but not Bk(IV) in  $8M \text{HNO}_3$ – $0.5M \text{NaBrO}_3$ , working as a pre-filter to prevent Ce(IV) from contacting LN resin.

### **Dual Column (Cartridge) Preparation and Operations**

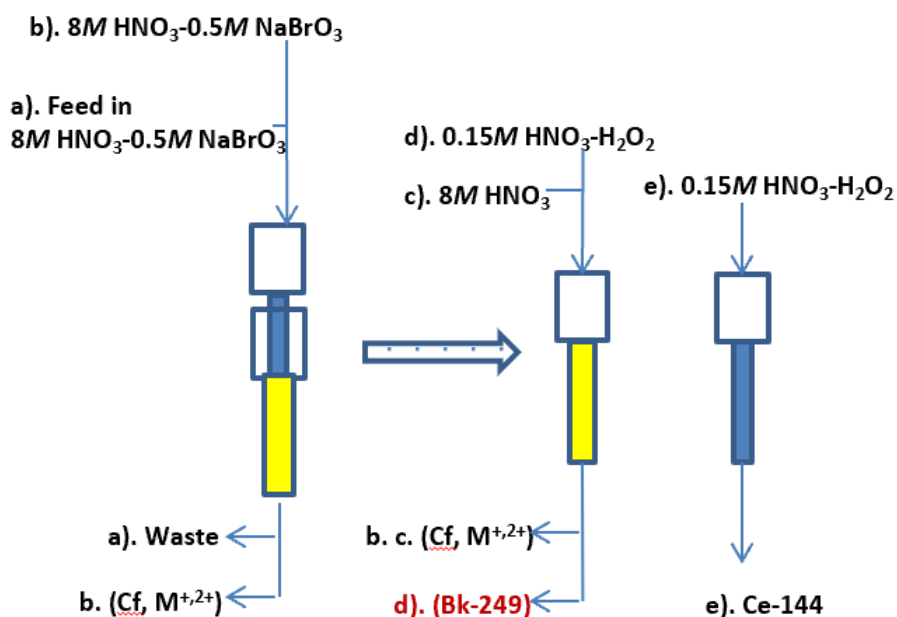


- LN resin cartridges or columns of varying volumes can be ordered from Eichrom, as well as empty cartridge/column trunk assemblies.
- MP-1 resin cartridge/column needs to be self-assembled by loading MP-1 resins (dry or wet) into the trunk (with frits at bottom and top) and then sealing the trunk top by snapping the top connector into the trunk.
- An LN cartridge, a MP-1 cartridge, and a syringe body are attached in a series (with no plunger into the syringe body).
- The general operations of such a dual column, after it is set up on a column stand, include the following:
  - Load liquid into the syringe body, then attach a plunger into the syringe and push the loaded liquid through in the order of MP-1 cartridge and then LN cartridge.
  - Once the plunger reaches the end of syringe, detach the syringe body from the cartridge before pulling the plunger out of the syringe body.
  - Reattach the empty syringe body to a cartridge if more liquid is to be loaded into cartridges, then repeat the operations of liquid loading, plunger pushing and syringe detachment.

### Reagents and Materials needed for $^{249}\text{Bk}$ Extraction from Analytical Samples

- A dual column, pre-conditioned with  $8M \text{ HNO}_3$  (often done before bagging-in).
- $8M \text{ HNO}_3$ – $0.5M \text{ NaBrO}_3$ , freshly prepared by adding  $2M \text{ NaBrO}_3$  into  $10.67M \text{ HNO}_3$  in a volume ratio of 1:3.
- $8M \text{ HNO}_3$ – $0.45M \text{ H}_2\text{O}_2$ ,  $0.15M \text{ HNO}_3$ – $0.45M \text{ H}_2\text{O}_2$ .
- $8M \text{ HNO}_3$ ,  $10.67M \text{ HNO}_3$ ,  $2M \text{ NaBrO}_3$  (from makeup area).
- **Samples** from campaign process for  $^{249}\text{Bk}$  analysis, **of known acidity** (to be adjusted into  $8M \text{ HNO}_3$ – $0.5M \text{ NaBrO}_3$ ) and a low enough content of total actinides (the assigned dual cartridge will allow a 10 mg level of total actinides, but analytical labs at REDC allow only much lower amounts of actinides).

### Diagram for Dual-Column Operation



### Dual Cartridge/Column Operation for $^{249}\text{Bk}$ Extraction

1. Fix and position the dual cartridge/column (already pre-conditioned with  $8M \text{ HNO}_3$ ) onto a column stand inside a glove box, or a hood if it meets the total activity limit requirement.
2. Prepare an  $8M \text{ HNO}_3$ – $0.5M \text{ NaBrO}_3$  solution of the desired volume by adding  $2M \text{ NaBrO}_3$  into  $10.67M \text{ HNO}_3$  in a volume ratio of 1:3. Prepare other required reagents if not prepared in advance.
3. Condition the dual cartridge/column: add three or more column volumes (CV) of  $8M \text{ HNO}_3$ – $0.5M \text{ NaBrO}_3$  solution (e.g.,  $2 \times 4$  or  $5 \text{ mL}$ ) into the empty syringe and push it through the dual cartridge/column (load twice since the syringe volume is only  $5 \text{ mL}$ ). Discard the effluent from the cartridge/column as waste.

4. First adjust the sample (or an aliquot of the sample) of known acidity into a 10.67M HNO<sub>3</sub> solution, then add 2M NaBrO<sub>3</sub> into this sample of 10.67M HNO<sub>3</sub> in a volume ratio of 1:3 to form a column feed of 8M HNO<sub>3</sub>–0.5M NaBrO<sub>3</sub> of desired volume (the preferred feed volume of a column is no more than ten column volumes, i.e., <20 mL feed for the dual cartridge/column. The smaller the feed volume, the better).

**Note:** *The feed of 8M HNO<sub>3</sub>–0.5M NaBrO<sub>3</sub> should be prepared no more than 20 minutes before feed loading to the dual cartridge/column.* The added NaBrO<sub>3</sub> oxidizes both the Bk and the Ce in the feed into tetravalent states, with NaBrO<sub>3</sub> reduced to red Br<sup>-</sup> and Br<sub>2</sub>, while radiation enhances the reduction of NaBrO<sub>3</sub> (higher radiation turns the feed into red faster).

5. Within ≤20 minutes, load the feed of 8M HNO<sub>3</sub>–0.5M NaBrO<sub>3</sub> into the empty syringe and push it through the dual cartridge/column (feeding more than 5mL in the volume requires multiple loading/pushing), collect the effluent from the cartridge/column into a bottle labeled “load,” which contains all mono-/di-/tri-valent impurities (with no tetravalent Bk, Ce, Pu, or Zr).
6. Elute the dual cartridge/column with 8M HNO<sub>3</sub>–0.5M NaBrO<sub>3</sub> totaling 15 mL (feed vial washes plus elution); collect the effluent into the load bottle as well.

(Tetravalent Ce, Zr and Pu are retained on the top MP-1 cartridge/column, while tetravalent Bk is adsorbed on the lower LN cartridge/column.)

7. **Detach the two cartridges/columns and put aside the MP-1 cartridge/column.** Fix and position the LN cartridge/column onto the column stand with an empty syringe attachment.
8. Add 5 to 10 mL of 8M HNO<sub>3</sub> to elute the NaBrO<sub>3</sub> from the LN cartridge/column (Bk stays on the LN cartridge during 8M HNO<sub>3</sub> elution), collect the effluent in a bottle labeled “elution.”
9. **Strip Bk off the LN cartridge/column** with 10 to 15 mL of 0.15M HNO<sub>3</sub>–0.45M H<sub>2</sub>O<sub>2</sub>, collect the strip in a bottle labeled “product.” This stripping of Bk is ready for <sup>249</sup>Bk analyses of α spec or mass spec.

**The MP-1 cartridge/column** can be disposed of as solid waste with adsorbed radioactive impurities. Or it can be stripped with 0.15M HNO<sub>3</sub>–0.45M H<sub>2</sub>O<sub>2</sub>, where Ce and Pu are off column, as well as part of the Zr.

10. The effluent (Bk) of 8M HNO<sub>3</sub>–0.45M H<sub>2</sub>O<sub>2</sub> from the LN column can be dried or adjusted to the desired form for α/γ /MS analyses.

**Note:** To drive red bromine out of waste/fraction solutions, gently heat the solutions in glass containers with a heating lamp and observe the red color fading (Br<sup>-</sup> → Br<sub>2</sub>↑).