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Separation of Thorium from Uranium Ore

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Abstract

Thorium-230 has many research applications, but there is not a commercial source of this isotope. However, since ^{230}Th is part of the ^{238}U decay chain, it can be separated from naturally occurring uranium. In this work, a novel procedure was developed to separate thorium from uranium ore, consisting of leaching, liquid-liquid extraction, precipitations and ion exchange chromatography. The final product was 91.32 ± 0.77 mg of thorium with a purity of 99.5 ± 1.2 wt. %. Of that, 7.65 ± 0.10 mg was ^{230}Th and the remainder ^{232}Th . The total yield of ^{230}Th was 71.1 ± 5.4 %. Ways to improve the yield by further processing the back-extraction solution are suggested.

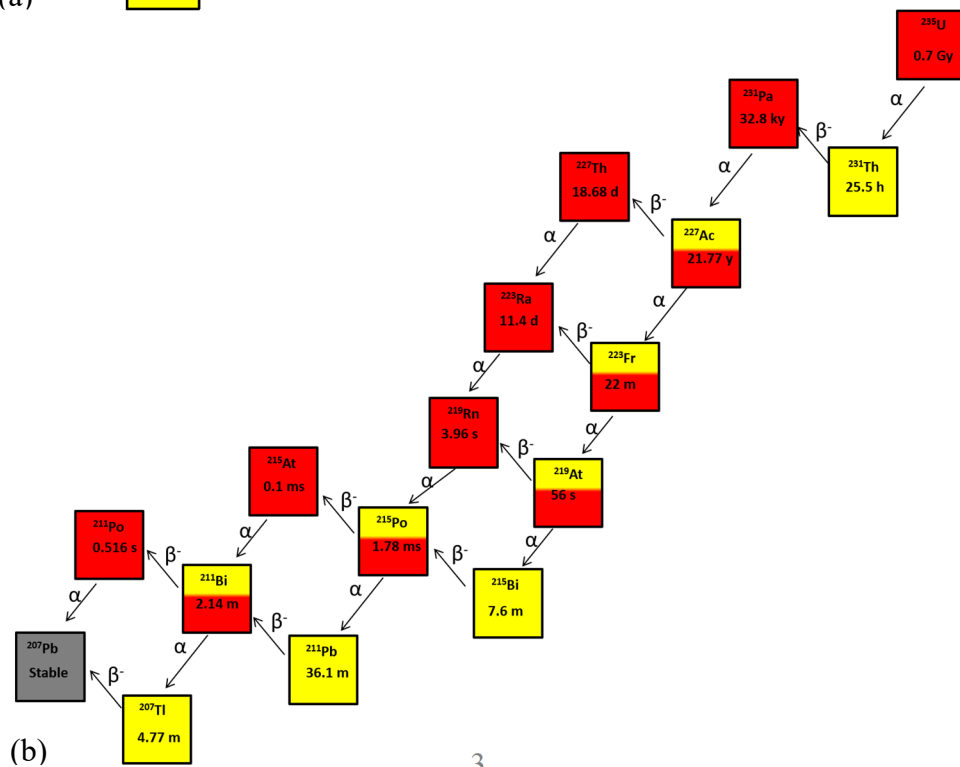
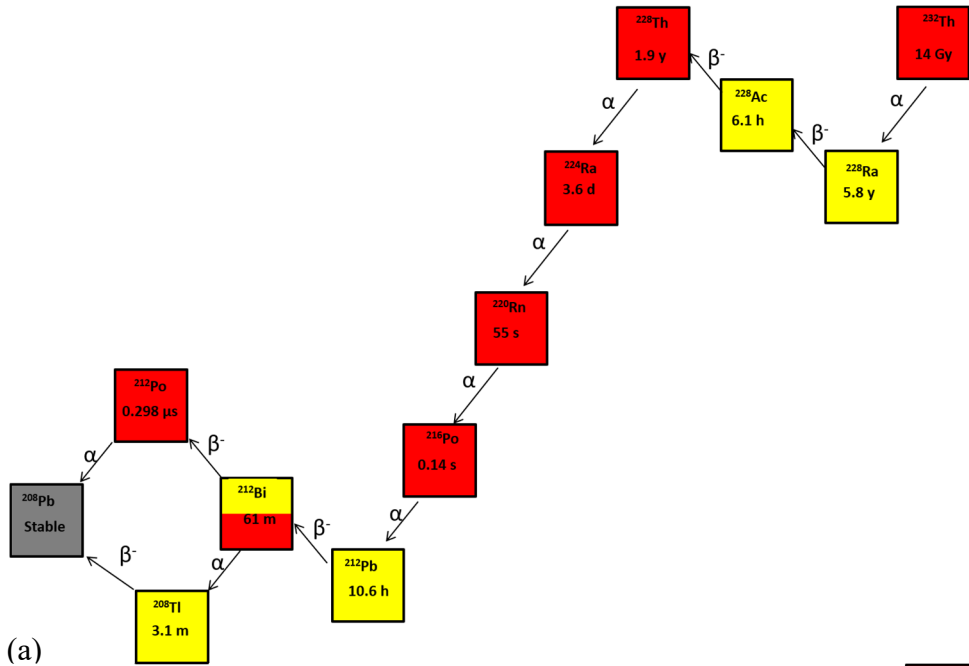
Keywords

Uranium ore, ^{230}Th , liquid-liquid separation, ion exchange chromatography

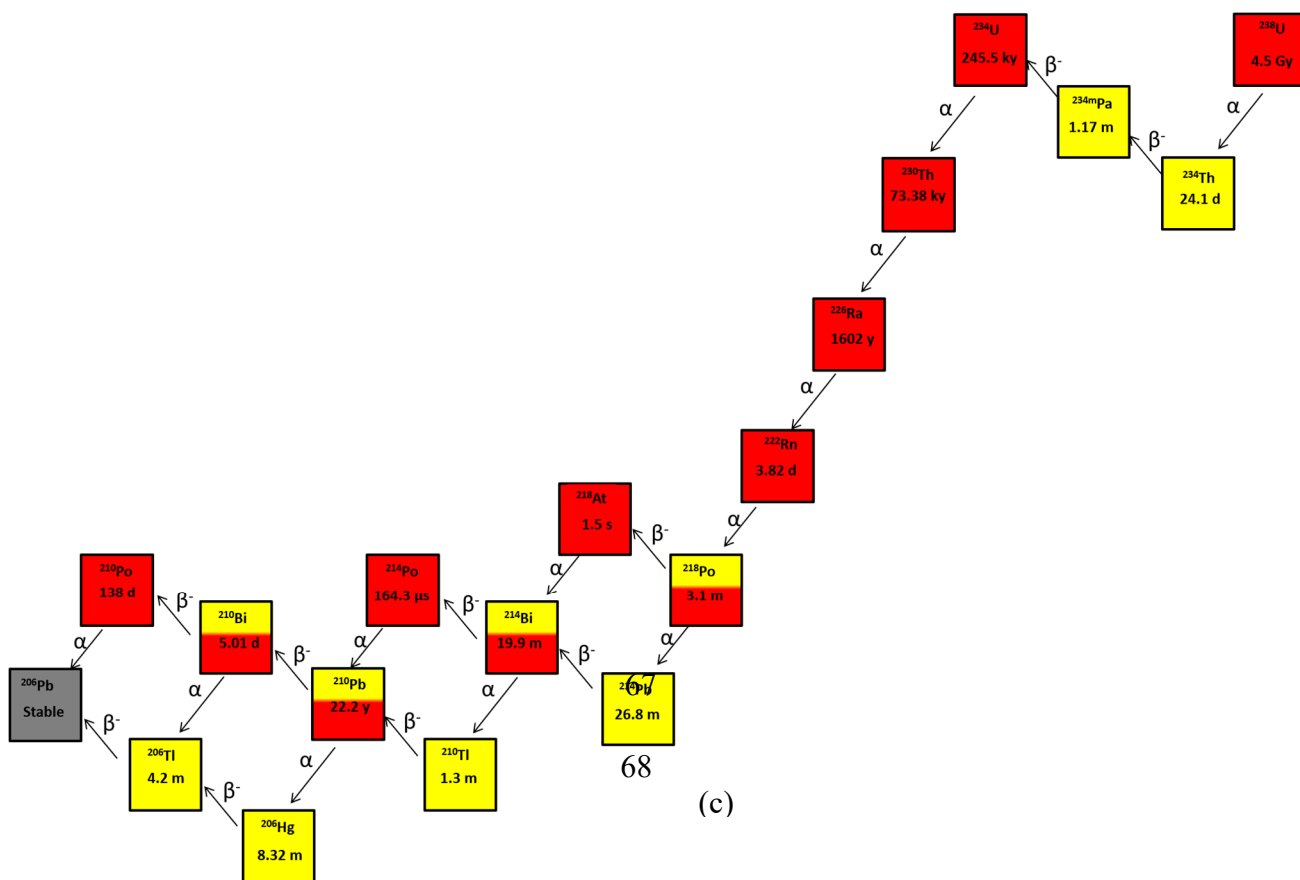
Introduction

Thorium-230, historically known as ionium, is part of the ^{238}U decay chain (see Fig. 1). There are many research areas today where this isotope is relevant. It is an essential component of uranium-thorium dating which uses disequilibria between the parent isotope ^{238}U and its daughter ^{230}Th to date carbonate materials [1]. This dating method relies on the difference between highly soluble uranium and slightly soluble thorium, which can lead to their separation during geological processes [1]. Recent work has also been done to better characterize ^{230}Th nuclear data to improve the accuracy of this dating method [2]. Improving ^{230}Th nuclear data is also important for advanced thorium fueled fast reactor designs [3].

37 Thorium-230 has isotope production uses as well. Via the $^{230}\text{Th}(p,2n)$ reaction, it can be
 38 used to produce ^{229}Pa and its daughter ^{229}Th . Both of these isotopes have important
 39 research applications: ^{229}Pa is a pear-shaped nucleus that is a candidate for more sensitive
 40 studies on nuclear properties, like parity violation [4], and ^{229}Th is a medically relevant
 41 isotope as it is the parent nuclide for ^{225}Ac , a potential agent for targeted alpha therapy
 42 (TAT) cancer treatment [5] [6].



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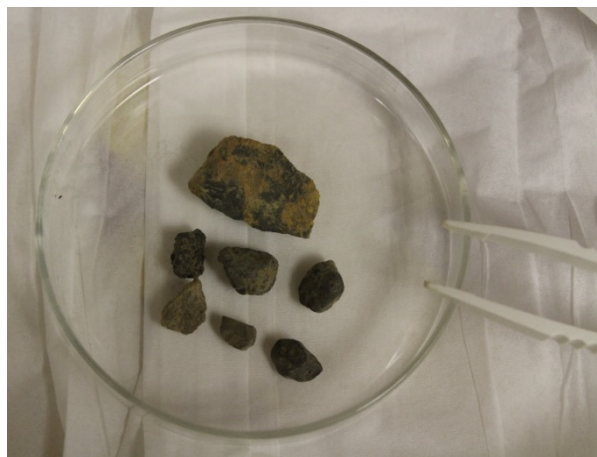
Fig. 1 Natural decay chains (a) ^{232}Th , (b) ^{235}U , and (c) ^{238}U .

Despite the interest in ^{230}Th for nuclear data measurements and isotope production, it is not available in sufficient quantities for research [7] [8]. This necessitates that it be obtained from the ^{238}U decay chain where it is naturally occurring. The purpose of this work is to develop a method for the extraction of ^{230}Th in significant quantities from uranium ore for use in nuclear data and isotope production experiments.

There has been work done in the literature to separate ^{230}Th from uranium mining waste streams [9] [10] [11] [12], but the chemical composition and concentration of thorium in a mining waste stream is far different than that in ore and most of these papers describe industrial scale purification and have limited relevance to the separation of thorium from unprocessed ore at the laboratory scale. The separation of milligrams of thorium from kilograms of unprocessed uranium ore has not been presented in the literature, and therefore, a novel process for this separation was developed.

83 Uranium ore is classified by grade, with high-grade ore containing 1 to 4 wt. % uranium,
84 medium grade with 0.1 to 0.5 wt. % uranium and low-grade with less than 0.1 wt. %
85 uranium [13]. Uranium is often found as uranite (previously known as pitchblende) in
86 high-grade ores, which contains mixed uranium oxide compounds [13] [14]. Lower-
87 grade ores can have a number of different uranium containing minerals; in the United
88 States, vanadates and phosphates are common [13] [14].

89 The uranium ore used in this work is legacy material from Lawrence Livermore National
90 Laboratory (LLNL), and is extremely high-grade. The main components are quartz (α -
91 SiO_2), lead uranium oxide (PbU_3O_9), and uranium oxide (U_4O_9); clay
92 $((\text{Mg}_{11.06}\text{Fe}_{0.94})(\text{Si}_{5.22}\text{Al}_{2.78})\text{O}_{20}(\text{OH})_{16})$ and iron oxide ($\text{Fe}_5\text{O}_7(\text{OH}) \cdot 4\text{H}_2\text{O}$) are present in
93 smaller amounts. It was previously determined to have 39.1 ± 1.8 wt. % uranium by a
94 Davies and Gray titration and was characterized by mass spectrometry for trace element
95 analysis. Fig. 2 shows the ore as it was received. Relevant isotopic ratios were
96 determined with mass spectrometry; the $^{230}\text{Th}/^{232}\text{Th}$ ratio is 0.0922 ± 0.00150 and the
97 $^{235}\text{U}/^{238}\text{U}$ ratio is 0.0072579 ± 0.0000075 .



104 Fig. 2 Uranium ore.

105 Any natural source of uranium contains the three primordial actinide decay chains, ^{238}U ,
106 ^{235}U and ^{232}Th , and all of these have two thorium isotopes in their decay chains,
107 therefore, the final product will contain six thorium isotopes (see Table 1). Three of
108 these have half-lives less than a month (^{227}Th , ^{231}Th , ^{234}Th), and, therefore, can be reduced to
109 negligible amounts in the final product by allowing it to decay for a year as they will

110 have gone through more than 12 half-lives. This leaves $^{228}, ^{230}, ^{232}\text{Th}$ present in the final
 111 product, which cannot be altered without isotope separation; even though ^{228}Th has a
 112 half-life of 1.91 years [15], it is in secular equilibrium with ^{232}Th ($t_{1/2} = 1.4 \times 10^{10}$ y) so
 113 the amount cannot be reduced by waiting for it to decay. However, ^{228}Th and ^{232}Th are
 114 well characterized isotopes in regard to nuclear data [15] and should not significantly
 115 interfere with the previously mentioned uses for ^{230}Th .

116 Table 1 Naturally occurring thorium isotopes. Half-lives from Ref. [15].

Primordial Actinide	Thorium isotopes in decay chain	Half-Life
^{238}U	^{234}Th	24.10 d
^{238}U	^{230}Th	75,380 y
^{235}U	^{231}Th	25.52 h
^{235}U	^{227}Th	18.68 d
^{232}Th		1.405×10^{10} y
^{232}Th	^{228}Th	1.9116 y

117 In the uranium mining industry, ore containing uranium is first leached to dissolve out the
 118 uranium [14]. The leaching process can be done under acidic or alkaline conditions, and
 119 uses the solubility of uranium(VI) as a sulfate or a carbonate [13] to dissolve the uranium
 120 into sulfuric acid or a sodium carbonate/bicarbonate solution, respectively [14]. In either
 121 case, if the ore contains uranium(IV), which has limited solubility, an oxidant is added to
 122 convert it to uranium(VI), which is highly soluble in the aforementioned solutions [13]
 123 [14]. Common oxidants are iron, manganese dioxide (MnO_2), and hydrogen peroxide
 124 (H_2O_2) [13] [14]. Leaching is followed by more selective purification methods, like
 125 solvent extraction or ion exchange chromatography, to remove other elements and
 126 minerals that also dissolve under the leaching conditions [13] [14].

127 Acidic leaching is generally preferable as it is faster and requires fewer processing steps
128 than alkaline leaching, which is only used under very specific conditions when the
129 minerals in the ore have a high acid consumption; therefore, it was decided to do acidic
130 leaching for this experiment [14]. However, it was not desirable to use sulfuric acid in
131 this process for several reasons. Sulfuric acid is time-consuming to evaporate, has a high
132 density, high viscosity and very low pH, requiring large volumes of base for
133 neutralization. In addition, uranium sulfate forms more favorably than thorium sulfate,
134 so this method is not optimal for thorium recovery. All of these factors make sulfuric
135 acid unfavorable for leaching thorium, particularly in a non-industrial setting. Therefore,
136 for this work, an entirely novel, multi-step leaching procedure using nitric acid (HNO₃)
137 was developed as an alternative to the once-through sulfuric acid-based leaching, which
138 is common in industry.

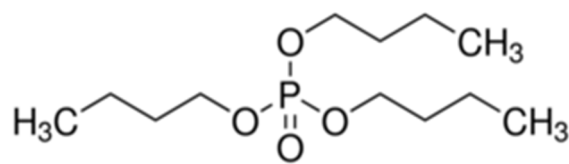
139 A liquid-liquid extraction was chosen as the first separation step to remove the thorium
140 from the bulk of the ore mass. Ion exchange chromatography and precipitation were
141 considered but not practical for the first separation step due to the scale. While ion
142 exchange is extremely selective, very large ion exchange columns are needed for large
143 masses and these are not available in most non-industrial settings. Precipitation does not
144 work well when the masses are highly disparate, in this case since the uranium is by far
145 the largest mass component in the solution, precipitating uranium would likely carry the
146 other actinides, or carrier would need to be added to precipitate thorium, which would
147 add mass to the system and create the same problem in the next processing step.

148 Liquid-liquid extraction is ideal because it can be highly selective and can significantly
149 reduce mass for later separation steps. For this experiment, tributyl phosphate (TBP), see
150 Fig. 3, was chosen as the extractant.

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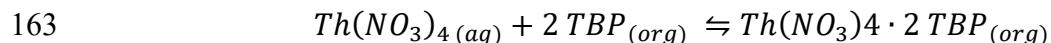
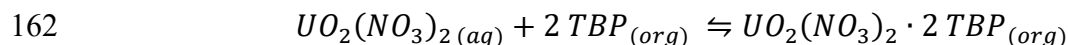
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Fig. 3 Tri-butyl phosphate.

157 The extraction of uranium, and thorium from aqueous solutions with TBP has been
158 extensively studied in the literature [16] [17] [18] [19] [20] [21]. TBP extractions are
159 commonly applied to ore processing as well, see Refs. [9] [10] [11] [12]. In HNO₃-TBP
160 systems, TBP complexes to uranium and thorium, as shown below [16], and extracts
161 them into the organic phase, separating them from the other constituents of the ore.



164 The literature gives a variety of conditions for extracting thorium from aqueous HNO₃
165 solutions of uranium ore waste: Ref. [10] recommends an aqueous phase of 1 M HNO₃
166 with 8 M total nitrate with 30% TBP in kerosene as the organic phase, Ref. [9] used 0.4
167 M HNO₃ with pure TBP and Ref. [12] recommends oxalic acid (C₂H₂O₄) with pure TBP
168 for a high yield extraction and 0.4 M HNO₃ (3 M total nitrate) with pure TBP for a
169 sufficient extraction.

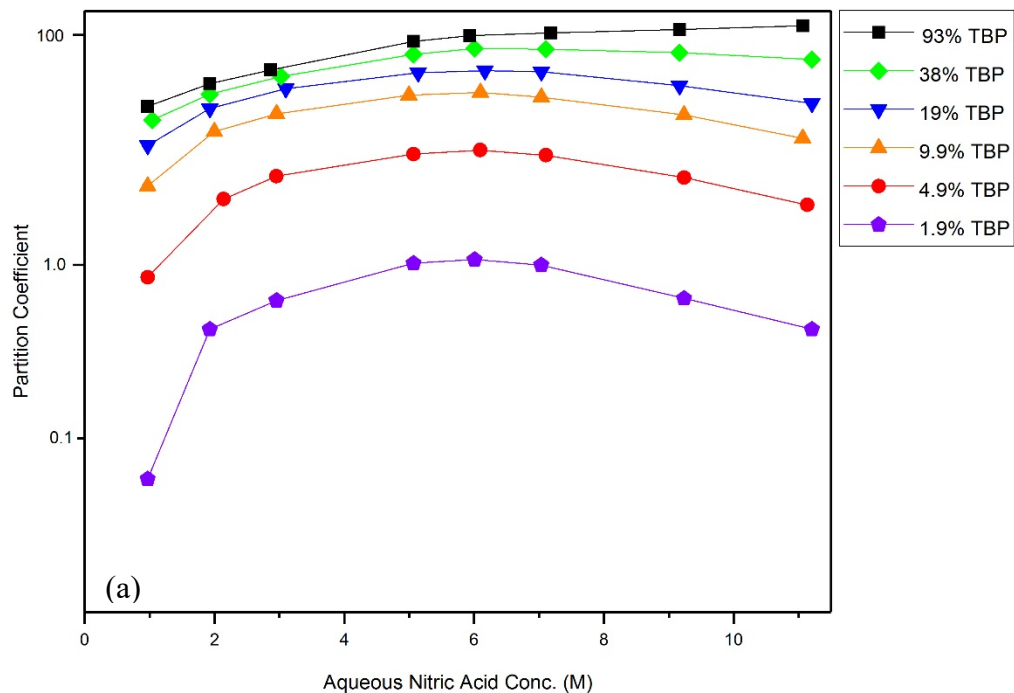
170 Reference [16], which presents a comprehensive study of thorium extraction by TBP, was
171 used as a basis for the forward-extraction in this work because it was desirable to extract
172 the thorium directly from the conc. HNO₃ leaching solution rather than dilute to a lower
173 HNO₃ concentration to keep volumes to a minimum. Although Ref. [16] is limited to
174 concentrations from 1 to 11 M HNO₃ (see Fig. 4), the procedure outlined in this paper
175 was tested with conc. HNO₃ as the aqueous phase and performed extremely well, it was
176 therefore used to determine the conditions for the liquid-liquid extraction in this
177 experiment, particularly diluent concentration and relative phase volumes. However, the
178 procedure ultimately developed for the bulk liquid-liquid separations has not been
179 reported in the literature in the volumes or concentrations that were used in this process.

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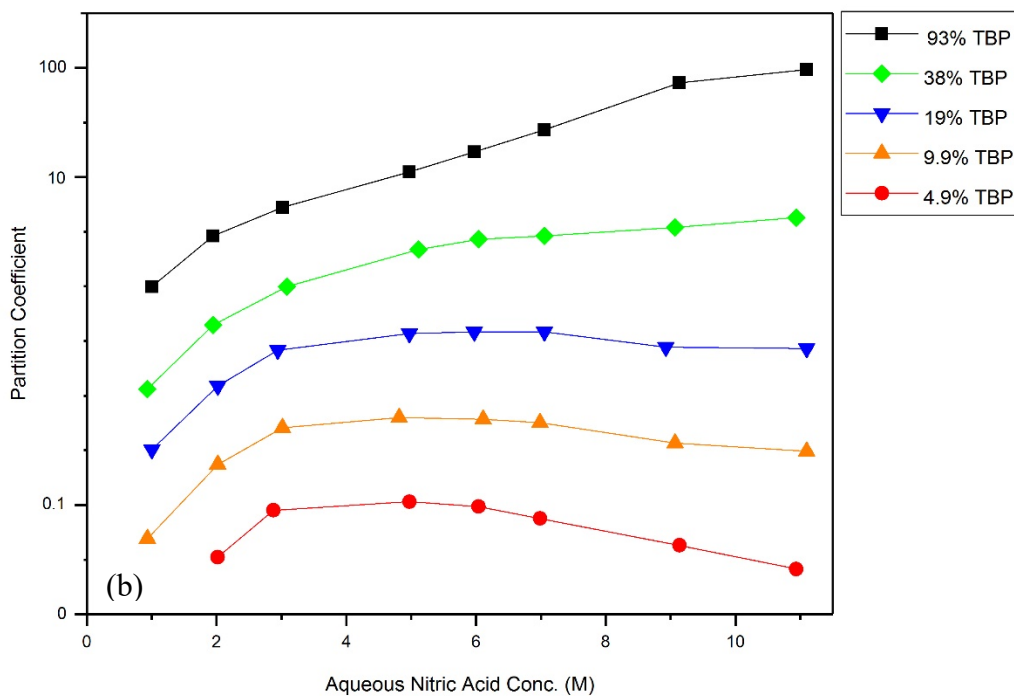
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202 Fig. 4 Partition coefficients of uranium (a) and thorium (b) in HNO₃. Data from Ref.
203 [16]; the diluent was kerosene.

204 As with the extraction from aqueous solution into TBP, the literature gives a variety of
205 ways to back-extract the thorium and uranium from TBP into an aqueous solution. Ref.
206 [16] suggests back-extraction of thorium with 6 M hydrochloric acid (HCl), while Ref.
207 [9] uses 1 M hydrofluoric acid (HF) and Ref. [10] uses 0.1 M HNO₃. The options for
208 uranium back-extraction are similarly varied with Ref. [16] using 10 wt. % ammonium
209 carbonate ((NH₄)₂CO₃), while Ref. [17] suggests 3 M acetic acid (CH₃COOH). For this
210 experiment, many options for the aqueous phase were considered and tested on a small
211 scale, ultimately, HF was chosen as the aqueous phase for the back-extraction based on
212 Ref. [9]; initial tests with HCl and HNO₃ back-extractions had low to no yield of thorium.

213 Once the thorium and uranium are separated from the bulk mass, an anion exchange
214 column was used for a more selective separation. Anion exchange was chosen rather
215 than cation exchange because thorium tends to bind irreversibly to cation exchange resins
216 due to slow kinetics and an extremely high distribution coefficient. It displays similar
217 behavior on anion exchange resins in HF as well. Finally, since the back-extraction
218 solution contains a significant amount of the uranium mass, an optimal separation system
219 would bind the thorium, a much smaller mass, and allow the uranium to pass through the
220 column thus decreasing the amount of resin needed.

221 Considering these conditions, the column separation used in this experiment was based
222 on the thorium-uranium separation in Ref. [22], which loads uranium and thorium in 8 M
223 HNO₃ on a Dowex 1x8 column.

224 **Experimental**

225 The ore for this experiment is described above. Before processing it was dry-crushed
226 with a ball mill (see Fig. 5). All chemicals were purchased from Sigma-Aldrich and were
227 ACS grade or higher; acids were diluted as necessary with Millipore Milli-Q deionized
228 water (18.2 MΩ cm). All mass spectrometry measurements were performed with a
229 Thermo Scientific iCAP quadrupole ICP-MS. Full quantitative analysis was done with a
230 linear calibration curve based off external standards. An internal standard was used to

231 correct for matrix signal suppression and instrument drift. Samples were analyzed in
232 triplicate and the reported error is the standard deviation of the measurements. A high
233 purity germanium (HPGe) gamma-ray spectrometer with Ortec NIM electronics and
234 ASPEC multi-channel analyzer was used to monitor the ore processing in several steps
235 and to make relative measurements. *Maestro software* (Ortec) was used to analyze the
236 resultant spectra and all measurements were made using the same HPGe detector and in
237 the same geometric configuration. Quantitative gamma spectroscopy was performed by
238 the nuclear counting facility at LLNL.

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Fig. 5 Uranium ore after ball-milling.

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Leaching

245 A sequential leaching process was developed to remove the elements of interest from the
246 ore. Three tests of novel leaching methods were done on a small sample of ore and the
247 most efficient was scaled up for bulk processing.

248 The initial leaching tests were done simultaneously under identical conditions comparing
249 the leaching efficiency of conc. HNO_3 , conc. HCl and aqua regia. Each used 20 g of ore
250 in a Teflon beaker. The solution for each step was allowed to react for 24 hours total and
251 between steps the solutions and remaining ore/precipitates were centrifuged for 2 minutes
252 and 10 seconds at 4500 rpm. The solution was then decanted and the solid was dried at
253 95°C for 2.5 hours before the next solution was added.

254 Initially, 20 mL of the acid solution of interest was added to each beaker and heated at 80°C
255 on a hot plate for six hours under observation. An additional 20 mL of acid was
256 added after 3 hours. Initially, it was observed that the HNO_3 beaker bubbled and evolved
257 a significant amount of brown gas, identified as NO_2 , and the solution was dark yellow.

258 The HCl beaker turned forest green with no gas emission or bubbles. The aqua regia
259 beaker was dark yellow-green, violently fizzed and evolved brown gas. After heating
260 the beakers sat for 18 hours, after which it was seen that the HNO₃ beaker had the least
261 amount of ore mass remaining, a yellow solution and a white precipitate. The HCl
262 beaker had leached the least, with a significant amount of ore mass remaining, along with
263 a dark green solution and black precipitate. The aqua regia beaker was between the other
264 two with some ore mass remaining, a yellow-green solution and white and black
265 precipitate present.

266 For the second step, 1 mL of unstabilized H₂O₂ was added to serve as an oxidant and
267 allowed to react for 3 minutes before the addition of 25 mL of the initial acid. After the
268 leach was completed, the aqua regia beaker was observed to have the most solid
269 remaining; due to this and the initially more vigorous reaction (the fizzing was judged to
270 be too risky on a large scale) this method was disregarded without further testing. The
271 HNO₃ beaker again had the least amount of solid remaining, and the HCl beaker had
272 solid remaining at an amount between the HNO₃ and aqua regia beakers.

273 For the third step, 40 mL of conc HCl was added to the beaker that originally contained
274 conc. HNO₃ and 40 mL of conc. HNO₃ were added to the beaker that originally contained
275 HCl. This third leach was treated in the same manner as the first. The beaker that went
276 from conc. HNO₃ to conc. HCl had a dark green supernatant and a little solid remaining.
277 The beaker that had gone from conc. HCl to conc. HNO₃ had a yellow solution and not as
278 much dissolution; the remaining precipitate was black and white precipitate and pieces of
279 the initial ore were still visible.

280 Finally, the fourth step in the leaching test was another leach with the initial acids, this
281 time 30 mL. This was done in the same manner as the previous steps, and after the leach,
282 the HNO₃ beaker had a pale-yellow solution and white precipitate, which contained Pb
283 and Ra (identified by gamma spectroscopy). The HCl beaker was green with a black
284 precipitate and some white precipitate and ore remaining.

285 From these results, a final leaching procedure consisting of four steps was established for
286 use with the bulk ore. The total mass of ore processed was 1.7 kg. It was done in five

287 batches each in a 4-L glass beaker; three of the beakers had about 400 g each of ore and
288 the other two contained about 200 g each of ore. For each step in the leach process, the
289 solution was mixed with a stir bar for 48 hours then, after the reaction was complete, the
290 solution was removed with a peristaltic pump and the ore dried overnight (65 to 80 °C).

291 Leach one used 2.5 L of conc. HNO₃ for the beakers with 400 g ore and 1.5 L of conc.
292 HNO₃ for the beakers with 200 g ore. This was an extremely exothermic reaction and
293 acid was added carefully over the course of about two hours. After all the acid was
294 added, the solution was observed to boil under the reaction heat. A large amount of
295 brown gas, assumed to be NO₂, was evolved. The beakers were heated at 80 °C during
296 the second day for 8 hours. The resulting solution was dark yellow-brown, presumably
297 due to uranyl nitrate.

298 After removing the solution and drying the ore, as described above, the second leach
299 began. Leach two used 30 mL of unstabilized H₂O₂ initially and, after the reaction had
300 ceased, conc. HNO₃ was added to each beaker in the following volumes: 2.5 L to the
301 beakers with 400 g of ore and 1.5 L to the beakers with less mass. Gas was evolved
302 during this step as well, though not as much as in the first step; the solution was yellow,
303 again due to uranyl nitrate. Leach three used conc. HCl, 2 L for the beakers with more
304 mass and 1 L for the beakers with less. The solution was forest green; no gas or bubbles
305 were observed. Leach four used conc. HNO₃ with the same volumes as the third leach
306 step. The solution was pale yellow and no visible NO₂ gas was observed. Each step in
307 this process is shown in Fig. 6. Analysis was done with ICP-MS as described above and
308 gamma spectroscopy was done at the Nuclear Counting Facility at LLNL.

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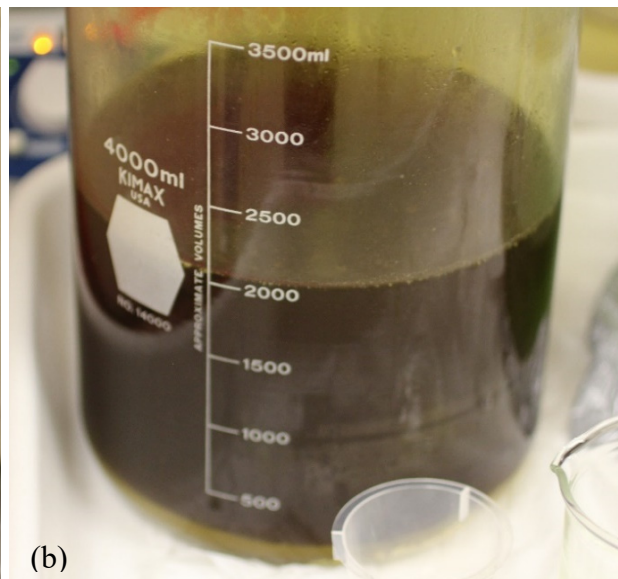
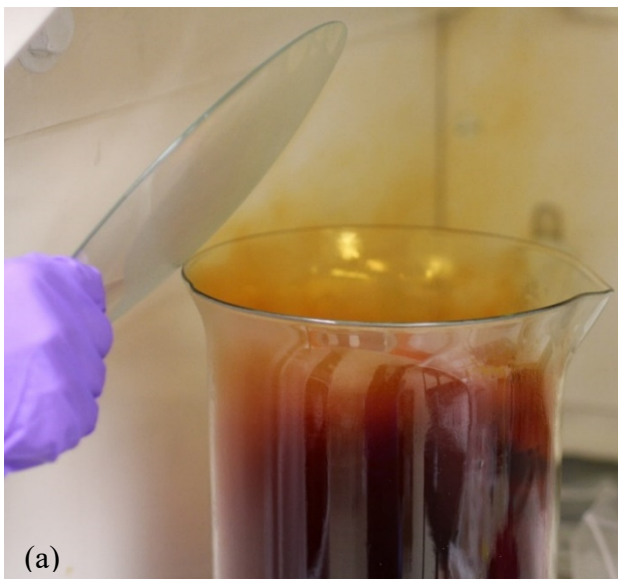
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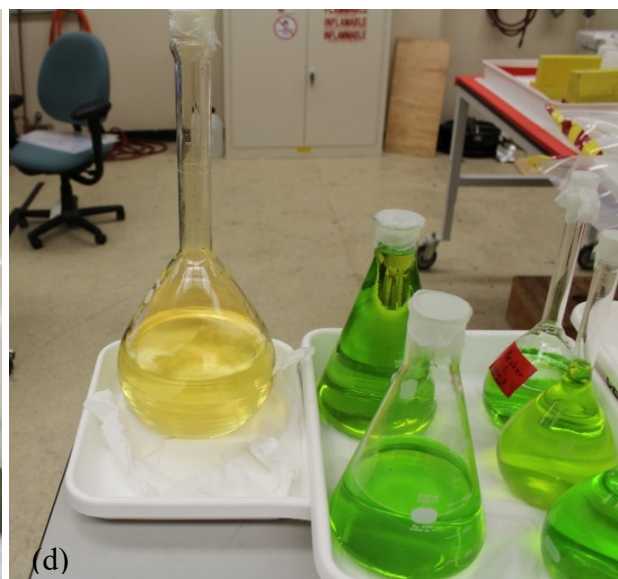
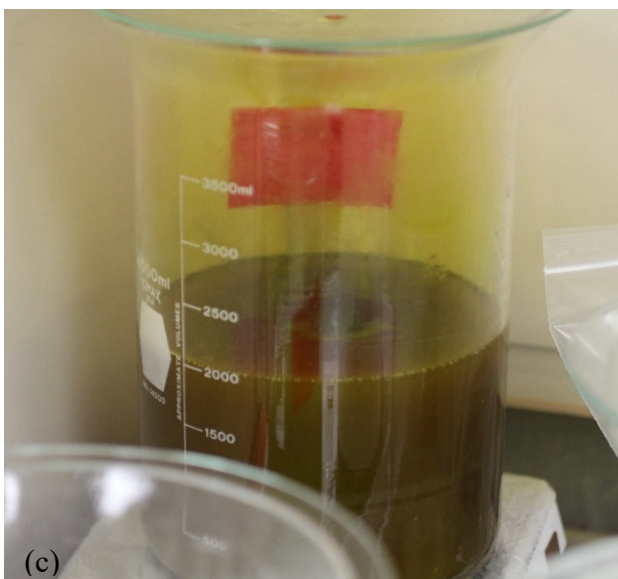
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331 Fig. 6 (a) Significant NO_2 gas evolution from adding conc. HNO_3 to ore in leach one (b)

332 Leach one (conc. HNO_3) after reaction has ceased (c) Leach two (H_2O_2 + conc. HNO_3)

333 while mixing. Note the reduction in gas evolution compared to leach one (d) Leach four

334 (conc. HNO_3) on the left and leach three (conc. HCl) on the right.

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336 **Liquid-liquid Extraction**

337 A liquid-liquid extraction was used to remove the thorium from the bulk ore. As leaches
338 one and two contained $90.8 \pm 15.4\%$ of the thorium initially present in the ore (see Fig.
339 10), only these two contained enough thorium to be worth further processing. The
340 extraction was tested on a small scale before being scaled up to treat the bulk solutions.
341 For these tests, a 20-mL aliquot of the first leach solution was added to a 50-mL
342 centrifuge tube containing an equal volume of 93% tributyl phosphate, which was diluted
343 with kerosene and preequilibrated with an equal volume of conc HNO₃ immediately
344 before the extraction. The phases were mixed by manually shaking for 10 minutes then
345 separated by centrifugation (2000 rpm, 4 minutes) and the organic phase removed by
346 pipette. Each phase was counted by gamma spectroscopy. The back-extraction was
347 tested with several different aqueous phases: 10% wt. ammonium carbonate, 3 M acetic
348 acid, 0.2 M HNO₃, 1 M HF, dil. HCl, dil. HNO₃. For each test, the organic phase was
349 back-extracted with an equal volume of aqueous phase in the same manner as the
350 forward-extraction. The back-extraction with 1 M HF had the best results for thorium.
351 The full extraction process was repeated eight times on 20 mL aliquots to characterize the
352 percent extraction.

353 Based on these results, a procedure was developed for the bulk extractions. First, 750 mL
354 of the leach solution was added to a 2-L Nalgene separatory funnel, then 750 mL of 93%
355 TBP in kerosene (pre-equilibrated with an equal volume of conc. HNO₃) was added.
356 This was mixed for two hours with a Heidolph overhead mixer equipped with a propeller
357 type stirring rod made of Teflon coated stainless steel. The mixed phase separated under
358 gravity overnight; 12 hours was the minimum time for phase separation. The aqueous
359 phase for the forward-extraction was removed and 750 mL of 1 M HF was added. This
360 was mixed for two hours with a 12-hour phase separation time. The HNO₃ phase and
361 organic phase were discarded after processing. Phase separation for the forward-
362 extraction and back-extraction is shown in Fig. 7(a) and 7(b), respectively. Analysis for
363 the back-extraction solution was done with ICP-MS as described above.

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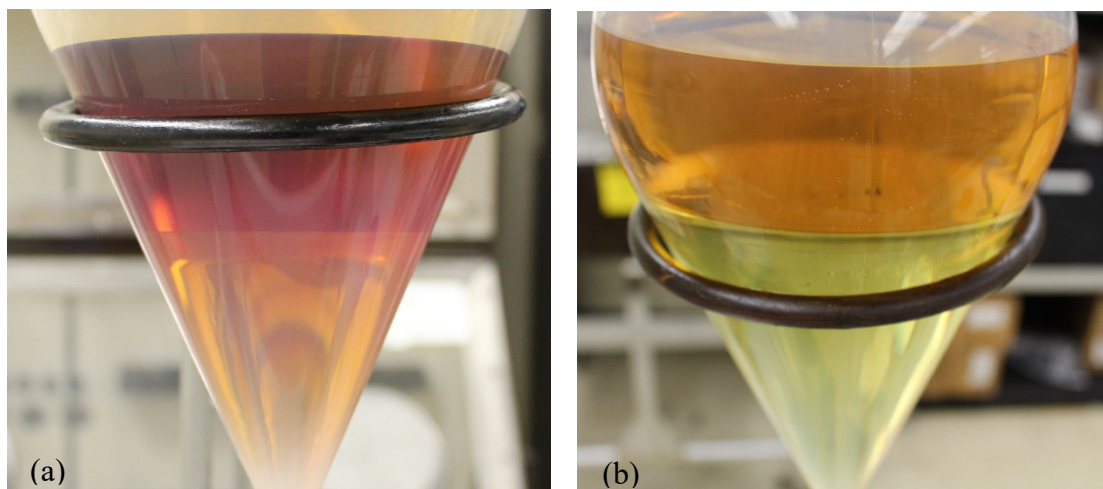
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374 Fig. 7 (a) Forward-extraction phase separation (TBP organic phase on top; HNO₃ aqueous
375 phase on bottom), (b) Back-extraction phase separation (TBP organic phase on top; HF
376 aqueous phase on bottom).

377 Precipitation and Ion Exchange Chromatography

378 The back-extraction solution in 1 M HF was centrifuged to remove thorium tetrafluoride
379 (ThF₄), which precipitates, although not quantitatively. This is a white, highly insoluble
380 salt; gamma spectroscopy determined that some uranium and protactinium were carried
381 with the precipitate, which was dissolved into a nitrate solution composed of an equal
382 volume of sat. aluminum nitrate (Al(NO₃)₃·9 H₂O) and 8 M HNO₃. To this, sat. sodium
383 hydroxide (NaOH) was added until the solution had a pH of 14. This process precipitates
384 the actinides as hydroxides. The solution was centrifuged (4000 rpm, 2 minutes) and the
385 supernate was decanted. The supernate was discarded and the actinide hydroxides were
386 dissolved in conc. HNO₃. The dissolved hydroxide precipitate was analyzed with ICP-
387 MS.

388 This solution was divided into twelve, 40-mL aliquots and loaded into 5-mL (7.5 cm by
389 9.3 mm) Dowex 1x8 columns (100 – 200 mesh), pre-washed with eight bed volumes (40

390 mL) of 8 M HNO₃ to convert the resin to nitric form. The column was washed with 100
391 mL of 8 M HNO₃ to remove the transition metals, lanthanides, protactinium and uranium.
392 The thorium was stripped with 40 mL of 10 M HCl (Fig. 8). The thorium fractions from
393 all the columns were combined, evaporated to dryness and reconstituted in conc. HNO₃.
394 The final product was analyzed by ICP-MS and HPGe gamma spectroscopy.

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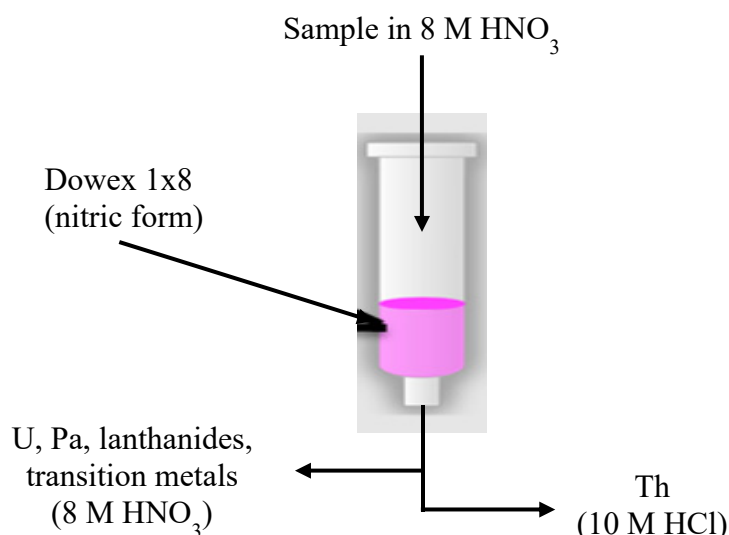
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Fig. 8 Schematic for HNO₃ anion column separation

403 For the ion exchange chromatography, a ²²⁷Th tracer was added to follow the progress of
404 the bulk thorium through the column as the main thorium isotopes present (²²⁸Th, ²³⁰Th,
405 ²³²Th) have no readily detectable gamma signatures and the naturally occurring ²²⁷Th had
406 already decayed out when the column separation was done. The tracer was separated
407 from legacy ²³¹Pa from LLNL. A schematic of the full separation process is shown in
408 Fig. 9.

409 The ²³¹Pa was initially in an aqueous acidic solution; the thorium and protactinium were
410 precipitated as hydroxides with NH₄OH while the rest of the ²³¹Pa daughters remain in
411 the supernate. The actinide hydroxides were washed with water, then dilute HNO₃,
412 which dissolves the thorium hydroxide into the supernate while leaving the protactinium
413 hydroxide as a solid. The thorium and protactinium were then separated by
414 centrifugation, and tracer spikes taken from the supernate.

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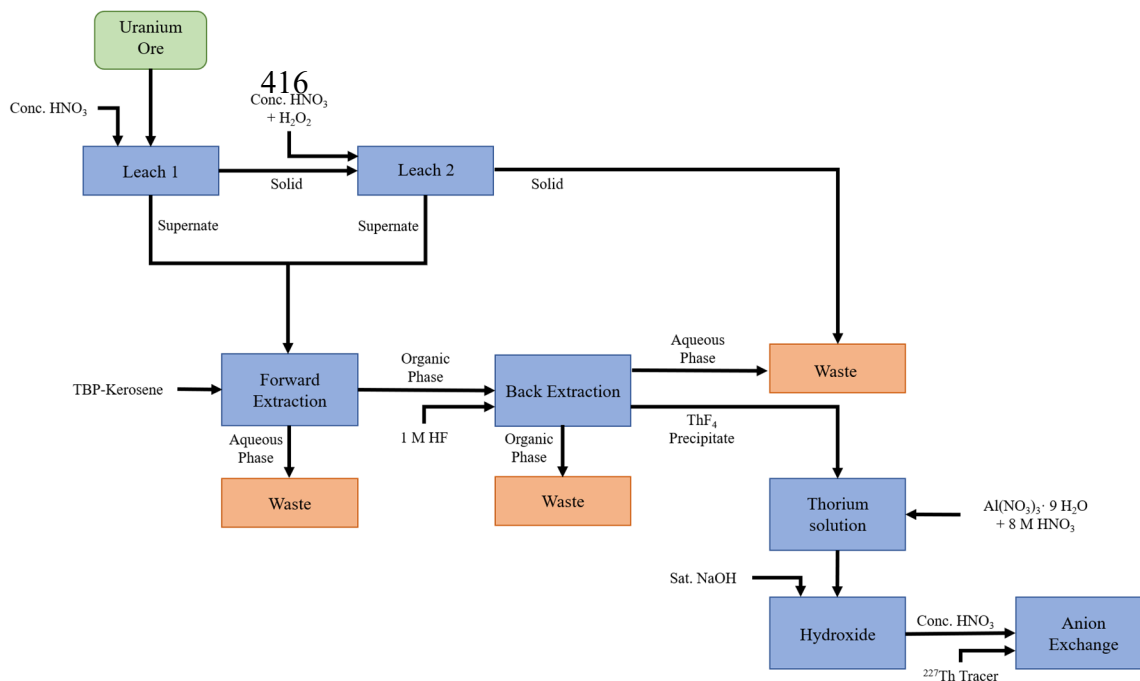


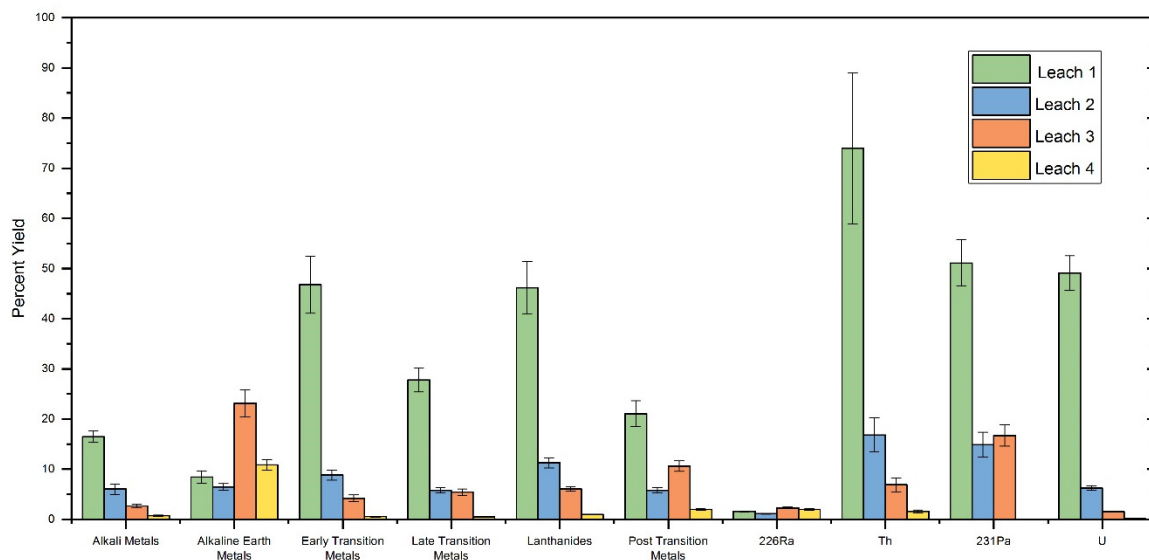
Fig. 9 Simplified chemical processing scheme.

Results and Discussion

Leaching

Yields for each leaching step were calculated from ICP-MS data for each leaching solution as compared to mass spectrometry data for the ore prior to processing. The calculated yields for each leach are shown in Fig. 10. For protactinium and radium, mass spectroscopy data was not gathered as these elements are prone to having interferences with the actinides. Therefore, gamma spectroscopy data is shown in Fig. 10 for ^{231}Pa and ^{226}Ra . The yields for uranium were calculated with both mass spectrometry and gamma spectroscopy (using the 185 keV line from ^{235}U); the results were within error. For Fig. 10 and all other mass spectrometry plots, the data has been simplified to show periodic trends rather than values for individual elements, see Supplementary Information for full mass spectrometry data.

439



440

Fig. 10 Ore leaching yields

441 From Fig. 10, it can be seen that thorium is leaching with a high yield in leaches one (74
 442 ± 15 %) and two (16.8 ± 3.4 %), and less well in three (6.9 ± 1.4 %) and four (1.57 ± 0.32
 443 %). The large error bars on the thorium yields are largely due to the error on the initial
 444 value for thorium in the unprocessed ore. The other actinides and the lanthanides also
 445 have high yields in the first leach along with some of the early transition metals,
 446 particularly scandium and yttrium (see Supplementary Information, Fig. 1). The early
 447 transition metals have a chemistry analogous to thorium in solution, so this behavior is to
 448 be expected. Thorium is stable in the 4+ oxidation state in solution and behaves like a d^0
 449 metal, giving it similar chemistry to the d^0 early transition metals like scandium, yttrium,
 450 and zirconium. This tendency for scandium and yttrium to follow thorium is seen in both
 451 the leaching and the liquid-liquid extraction; more selective methods are required to
 452 separate these metals.

453 The s- and p-block elements and late transition metals either do not form nitrate
 454 complexes as favorably or are bound in minerals that require harsher methods to dissolve,
 455 so these groups have much lower leaching yields.

456 Based on these results, as well as the time required to process the leaching solutions, only
 457 leaches one and two were selected for further purification, as mentioned previously.

458 **Liquid-liquid Separation**

459 Data for the TBP liquid-liquid separation for the initial, small-scale (20 mL)
 460 characterization appears in Table 2. The speciation of uranium and thorium in TBP is
 461 well known: two TBP molecules bond to the actinide in a trans fashion through the
 462 terminal oxo group on the phosphorus [23]. In the equatorial positions, thorium has four
 463 bidentate nitrate ligands and uranium has two trans bidentate nitrates and two trans
 464 terminal oxo ligands [23].

465 Table 2 Data for small-scale TBP liquid-liquid separation. Values are an average percent
 466 extraction for eight independent trials; the error is counting error.

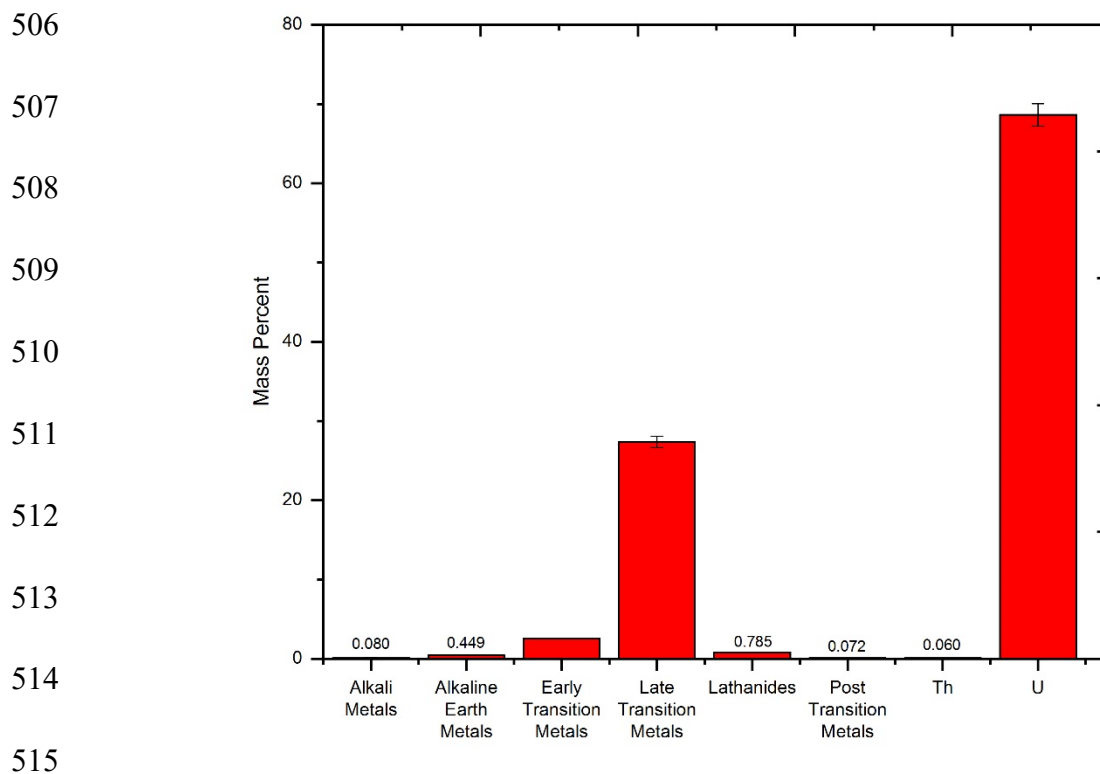
Element	Forward-Extraction (%)	Back-Extraction (%)
Th	98.01 ± 7.51	99.27 ± 7.21
Pa	98.89 ± 5.59	100.00 ± 3.46
U	76.59 ± 2.24	31.26 ± 1.85

467 It can be seen that the yields for thorium and protactinium are extremely high, while the
 468 yields for uranium are lower for both the forward- and back-extractions. These particular
 469 conditions were selected for high thorium yields, and it was expected for protactinium to
 470 act similarly under these conditions. This is because thorium and protactinium are both
 471 cations in solution and simply complex with the conjugate base of the acid. Uranium,
 472 however, exists as uranyl (UO_2^{2+}) in solution so the chemistry is different. This is
 473 particularly apparent in the back-extraction since thorium(IV) and protactinium(V) are
 474 both hard and highly Lewis acidic cations, while uranyl is softer and less acidic.
 475 Therefore, thorium(IV) and protactinium(V) complex very strongly to fluorides, which
 476 are hard and very Lewis basic, and have extremely high yields for the back-extraction,
 477 protactinium more so than thorium as it has a higher charge state but similar size making
 478 it harder and more Lewis acidic. Uranyl being softer and less acidic, does not complex as
 479 strongly to fluorides and subsequently has a low yield. Since the goal of the liquid-liquid
 480 extraction is to purify the thorium but also to remove mass from the system to simplify

481 later separations, the low extraction yields for uranium, one of the largest mass
482 components in the ore, is advantageous.

483 Mass spectrometry data for the back-extraction solution is given in Fig. 11. It should be
484 noted that this is taken from the back-extraction solution after removal of the ThF₄
485 precipitate and, therefore, is not representative of the extraction as a whole. The highest
486 mass concentrations in the back-extraction solution are iron ($27.3 \pm 0.71\%$) and uranium
487 ($68.6 \pm 1.4\%$). While this data cannot be considered quantitative due to the removal of
488 fluoride precipitate, from this data and the composition of the hydroxide precipitate (see
489 Fig. 13), it can still be seen that the back-extraction has largely separated the actinides
490 from the bulk of the ore mass. The main mass components in the back-extraction
491 solution are uranium and iron; all others are present at less than 2% by mass (see
492 Supplementary Information, Fig. 2). In the dissolved hydroxide precipitate, the mass
493 components are scandium, yttrium, lanthanides, thorium and uranium; all others are
494 present at less than 1% except aluminum, which was added by the chemistry. The
495 lanthanides, scandium and yttrium are well known to pass through TBP extractions with
496 the actinides. Furthermore, they all form low solubility fluorides and therefore tend to
497 follow ThF₄ precipitate. Uranium appears at a higher mass concentration in the back-
498 extraction solution than the precipitate, which is to be expected since uranyl fluoride is
499 highly soluble, unlike thorium tetrafluoride. Some uranium appears in the dissolved
500 hydroxide precipitate likely because some of the uranium is entrained in the ThF₄ mass,
501 not due to a co-precipitation.

502 Iron appears in the back-extraction solution and the hydroxide precipitate most likely
503 because it was present in such large amounts in the ore that even if only a few percent are
504 being held in the organic phase and subsequently by the ThF₄ precipitate by mass effects,
505 it would still be a significant amount.



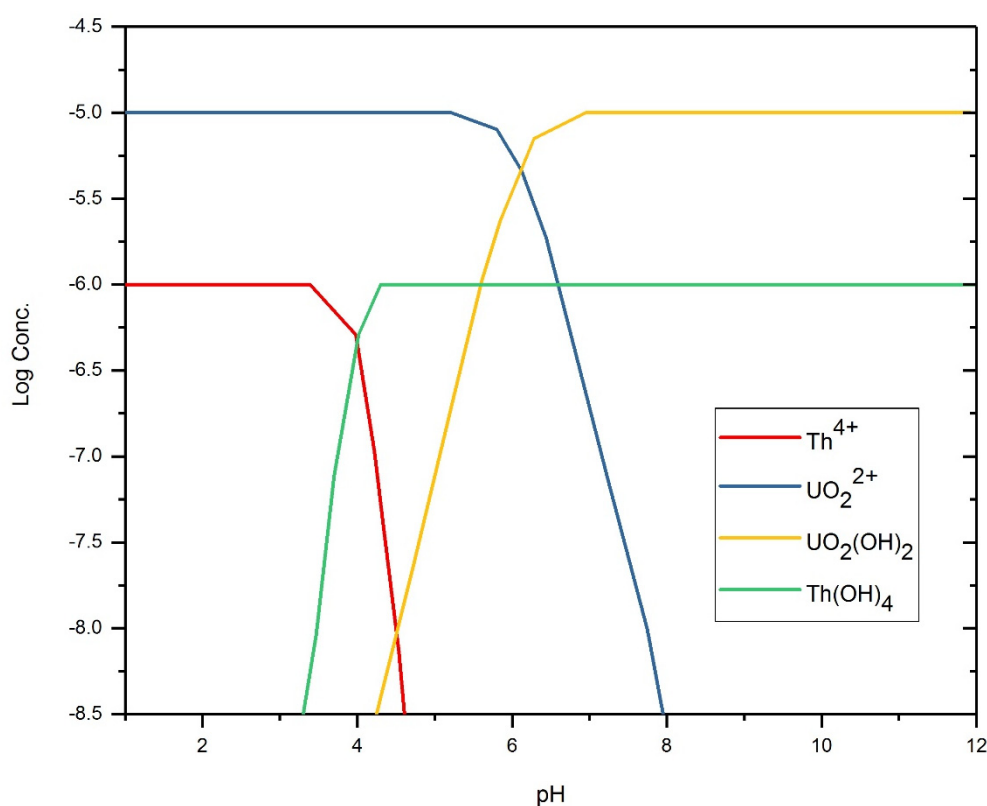
516 Fig. 11 Mass spectrometry data for the HF back-extraction solution after removal of ThF₄
 517 precipitate.

518 Precipitations

519 Thorium, like many actinides, has limited solubility in HF solutions and as a result, the
 520 back-extraction solution precipitates ThF₄, which can only be readily dissolved in
 521 solutions with a fluoride grabber, here Al(NO₃)₃·9 H₂O [24] [25]. The aluminum
 522 removes the fluorides from the actinides, converting them to nitrates with the production
 523 of aluminum difluoride (AlF₂⁺). This works well for thorium and the remaining uranium;
 524 however, protactinium is not converted to a nitrate in this process. This is evidenced by
 525 the behavior of protactinium later in the purification process: it elutes directly from the
 526 Dowex 1x8 anion exchange column, showing no affinity for the resin. If protactinium
 527 had been converted to a nitrate, it would elute only with sufficient washing as its
 528 distribution coefficient would be around 50 [26]. Protactinium(V) bonds very strongly
 529 with fluorides and it is very difficult to convert protactinium from a fluoride, so this
 530 behavior was expected. Since protactinium remaining as a fluoride simplifies the later

531 purification steps by minimizing the solution that must be eluted from the Dowex 1x8
532 column, no additional measures were taken to attempt to convert the protactinium to a
533 nitrate.

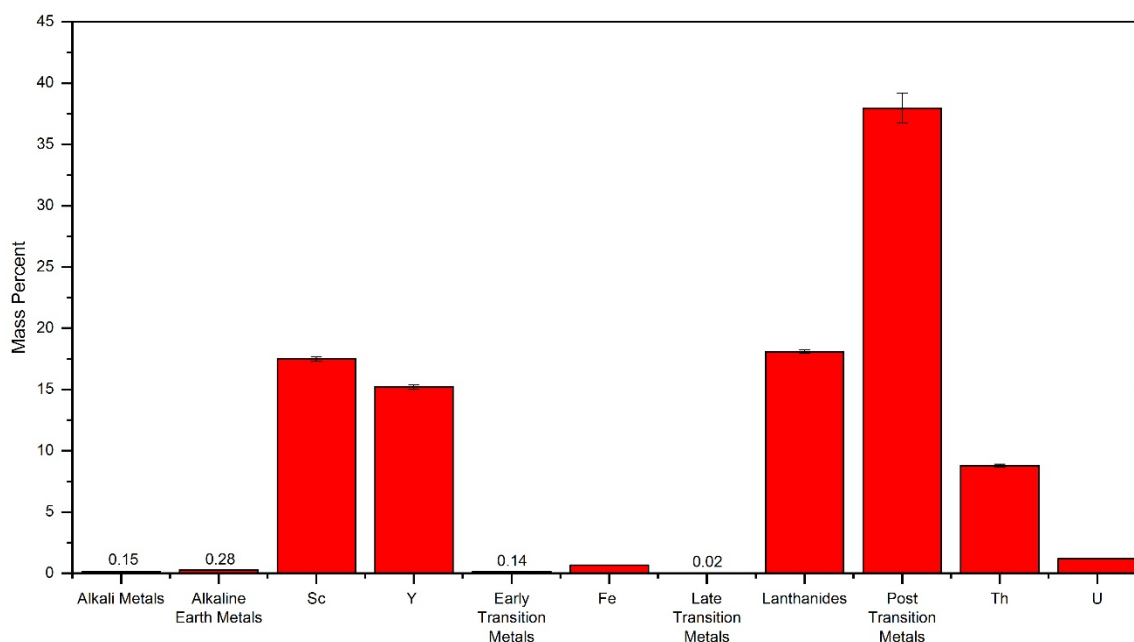
534 After dissolution in the nitrate solution, sat. NaOH was used to precipitate the actinides as
535 hydroxides. The speciation plot for this precipitation is shown in Fig. 12, as the pH
536 increases to above about 8, both uranium and thorium precipitate as hydroxides.
537 Thorium hydroxide has been noted in the literature to be a gelatinous precipitate and that
538 was observed here [25].



539 Fig. 12 Speciation of thorium and uranium in aqueous solution. Data from Ref.
540 [27].

541 The precipitation removes the actinides from the bulk of the aluminum mass, which
542 remains in the supernate as AlF₂⁺. The hydroxide precipitate was dissolved in conc.
543 HNO₃; mass spectrometry data for the dissolved hydroxide is shown in Fig. 13. Along
544 with thorium, uranium, scandium, yttrium, and iron are present in significant amounts
545 (see Supplementary Information, Fig. 3), having been carried in the ThF₄ precipitate and

546 then precipitating themselves as hydroxides. Scandium and yttrium in particular are
547 present in large amounts as they were present in the initial ore at a higher mass
548 concentration than thorium and have closely followed thorium throughout the processing.
549 Iron hydroxide precipitates under these conditions, it is often used as a carrier for
550 thorium, so it is present at a significant mass as well [25]. The post transition metals are
551 a large mass fraction solely due to aluminum, which was present in significant mass in
552 the solution and partially entrained in the hydroxide; the rest of the post transition metals
553 are present in negligible amounts. The behavior of protactinium was not quantitatively
554 accounted for in the precipitation as it was not measured with mass spectrometry. It was
555 visible with gamma spectroscopy, and since protactinium is readily carried during
556 precipitations [28], it is assumed to have been carried along with the other actinides as a
557 fluoride. It should be noted that Fig. 13 does not include data for sodium as it was
558 present in excess since NaOH was essentially serving as the solvent.

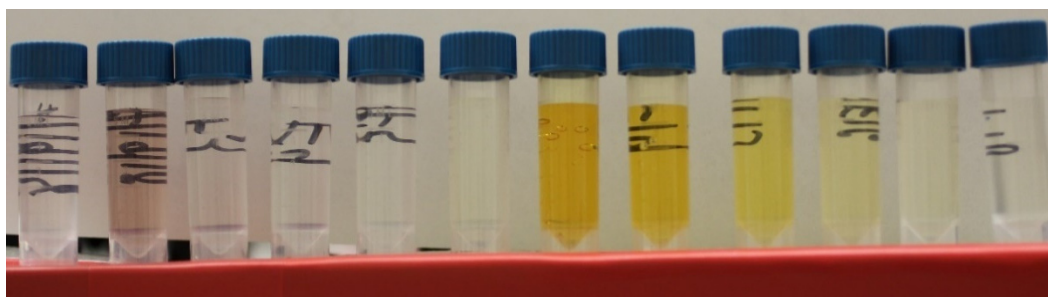


559 Fig. 13 Mass composition of dissolved hydroxide precipitate as determined by mass
560 spectrometry. Sodium not included.

561 Ion Exchange Chromatography

562 An ion exchange separation was done with Dowex 1x8 resin loaded in 8 M HNO₃. At
563 this concentration, the lanthanides and transition metals form cationic complexes and,
564 therefore, run through the column. The actinides (thorium, protactinium and uranium) all
565 have some affinity for the resin in nitrate form, though protactinium and uranium less so
566 than thorium, which bonds strongly as Th(NO₃)₆²⁻ [22] [29]. Therefore, sufficient
567 washing of the column with 8 M HNO₃ separates the thorium from uranium and
568 protactinium. As discussed previously, protactinium would have had a significant
569 affinity for the resin had it been converted to a nitrate; however it was observed to elute
570 immediately, indicating it was not converted from the fluoride to a nitrate or hydroxide in
571 the previous steps. The column was trialed on a small scale before the bulk processing
572 and the fractions are shown in Fig. 14.

573



574 Fig. 14 Fractions of HNO₃ Dowex 1x8 column. Transitions metals are eluted in the
575 second fraction causing the purple color. Thorium is eluted in the seventh fraction, which
576 appears yellow due to conc. HCl and conc. HNO₃ mixing on the column.

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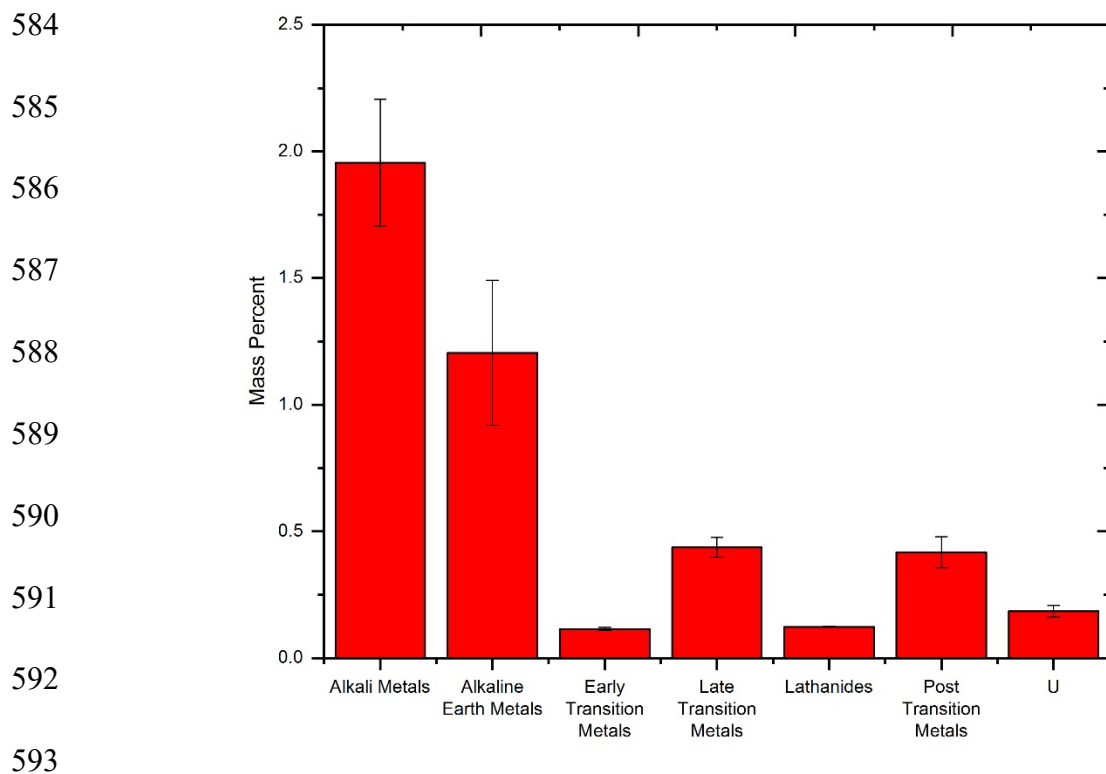


Fig. 15 Mass percentages of impurities in thorium product.

After the ion exchange column, the final product was 99.5 ± 1.2 wt. % thorium. The main impurities are alkali and alkaline metals along with iron and uranium. The impurities are shown by mass percent in Fig. 15. Sodium and aluminum, both used in the precipitation chemistry, dominate the alkali metals post transition metals, respectively, and explain the high mass concentrations of these groups (see Supplementary Information, Fig. 4). As before, protactinium is not included in mass spectrometry data due to interferences, however in the final sample there was no detectable ^{231}Pa . The total mass of thorium recovered was 91.32 ± 0.77 mg: 83.67 ± 0.76 mg of ^{232}Th and 7.65 ± 0.10 mg of ^{230}Th . The amount of ^{230}Th present in the ore initially can be calculated from the mass of uranium and $^{235}\text{U}/^{238}\text{U}$ ratio; this gives a result of 10.8 ± 0.8 mg ^{230}Th , indicating an overall yield of $71.1 \pm 5.4\%$ for thorium recovery. The yield can also be calculated based on mass spectrometry data for the initial ore, which measured 86.7 ± 17.7 mg of ^{232}Th . This indicates a yield of $96.5 \pm 19.8\%$, which is within error of the yield calculation for ^{230}Th , but with an extremely large error bar arising from uncertainty on the thorium mass concentration measured in the initial ore.

610 The main impact on the yield is the precipitation of ThF₄ from the back-extraction
611 solution. The leaching had an extremely high yield (about 90%) and the ion exchange
612 chromatography can be assumed to have a high yield as well as there was no detectable
613 thorium in the other fractions or remaining on the column. However, as shown in Fig.
614 11, there was some thorium remaining the in back-extraction solution after the
615 precipitation, which was not recovered. Therefore, the yield could be improved by
616 evaporating the remaining back-extraction solution to induce the precipitation of more
617 ThF₄, which could be treated in the same manner as described above. The remaining
618 solution could then be neutralized with NaOH to precipitate the actinide hydroxides,
619 which could be dissolved in conc. HNO₃ purified by ion exchange to separate the
620 constituents. However, since the research applications of ²³⁰Th do not require large
621 quantities of mass, the recovery in this work was determined to be sufficient, therefore,
622 further processing was unnecessary.

623 **Conclusion**

624 Thorium-230 has many research applications including radiometric dating and isotope
625 production. Despite being a long-lived and naturally occurring isotope, there is no
626 commercial source and, therefore, it must be acquired through separation from uranium
627 ore. A procedure to leach high-grade uranium ore and separate the thorium on a
628 laboratory scale was developed. This procedure developed and fully characterized a
629 sequence of HNO₃-based leaches followed by a liquid-liquid extraction from conc. HNO₃
630 using TBP-kerosene as the organic phase and HF for the back-extraction, which was done
631 with concentrations and on a scale not previously reported in the literature. From the
632 back-extraction solution, thorium was precipitated as ThF₄, then dissolved with
633 Al(NO₃)₃·9 H₂O and re-precipitated as a hydroxide. Finally, anion exchange
634 chromatography was used as a final purification step. The ultimate recovery of ²³⁰Th was
635 7.65 ± 0.10 mg, which is adequate for nuclear data and isotope production purposes. The
636 overall yield for ²³⁰Th was 71.1 ± 5.4%, which is largely due to a non-quantitative
637 precipitation following the liquid-liquid extraction. This could be improved by further
638 processing of the back-extraction solution; however, the yield obtained was sufficient for
639 future experiments.

640

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Supplementary information

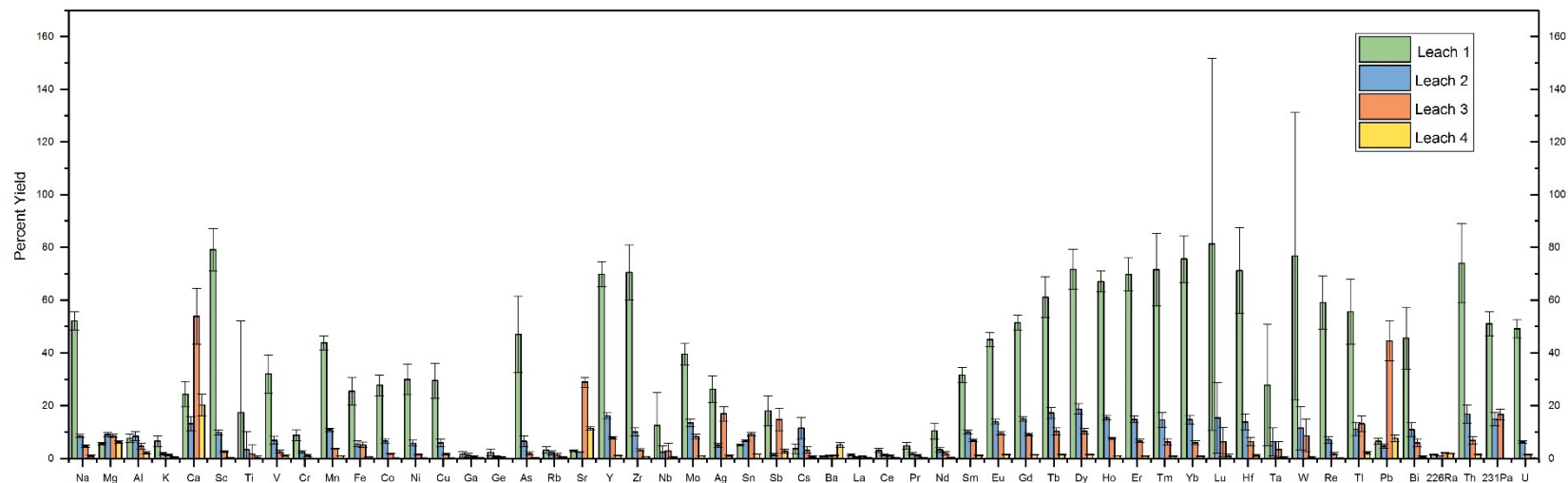


Fig. 1 Full mass spectroscopy data for leaching yields. For simplified figure in text (Fig. 10) elements have been categorized as alkali metals (Na, K, Rb, Cs), alkaline earth metals (Mg, Ca, Sr, Ba), early transition metals (Sc, Ti, V, Cr, Mn, Y, Zr, Nb, Mo, Hf, Ta, W, Re), late transition metals (Fe, Co, Ni, Cu, Ag), lanthanides (La-Lu), and post transition metals (Al, Ga, Ge, As, Sn, Sb, Tl, Pb, Bi); for each group the average leaching yield was calculated.

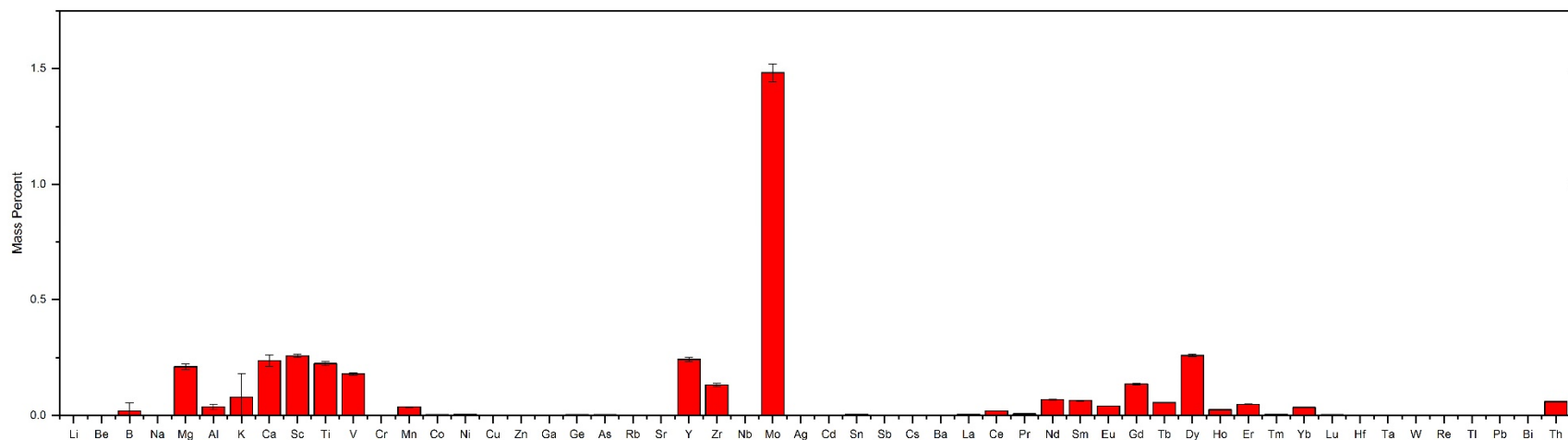


Fig. 2 Full mass spectrometry data for the back-extraction solution in 1 M HF; balance is iron ($27.3 \pm 0.71\%$) and uranium ($68.6 \pm 1.4\%$). For simplified figure in text (Fig. 11) elements have been categorized as alkali metals (Li, Na, K, Rb, Cs), alkaline earth metals (Be, Mg, Ca, Sr, Ba), early transition metals (Sc, Ti, V, Cr, Mn, Y, Zr, Nb, Mo, Hf, Ta, W, Re), late transition metals (Co, Ni, Cu, Zn, Ag, Cd), lanthanides (La-Lu) and post transition metals (B, Al, Ga, Ge, As, Sn, Sb, Tl, Pb, Bi); for each group the total mass percent was calculated

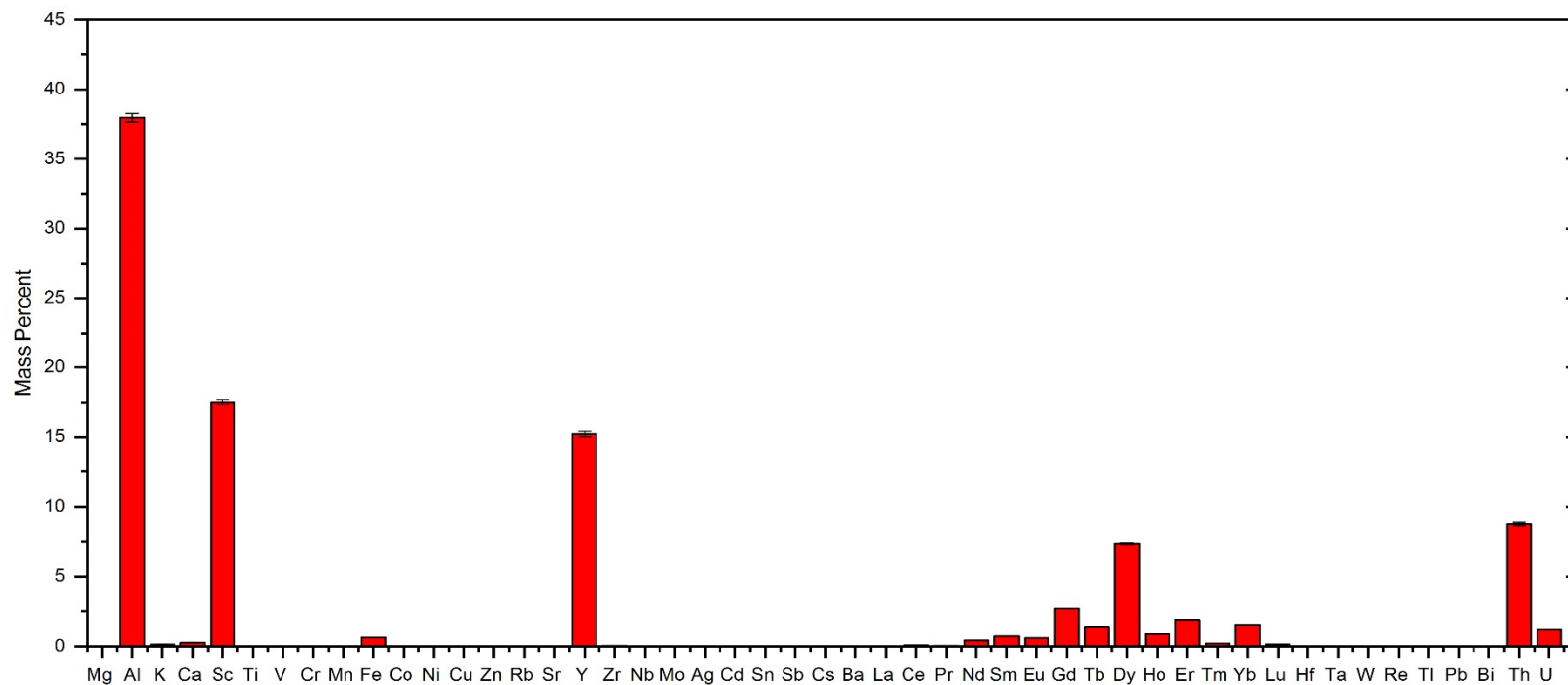


Fig. 3 Full mass spectrometry data for hydroxide precipitate dissolved in conc. HNO₃ acid. For simplified figure in text (Fig. 13) elements have been categorized as alkali metals (K, Rb, Cs), alkaline earth metals (Mg, Ca, Sr, Ba), early transition metals (Ti, V, Cr, Mn, Zr, Nb, Mo, Hf, Ta, W, Re), late transition metals (Co, Ni, Cu, Zn, Ag, Cd), lanthanides (La-Lu) and post transition metals (Al, Sn, Sb, Tl, Pb, Bi); for each group the total mass percent was calculated. Sodium not included.

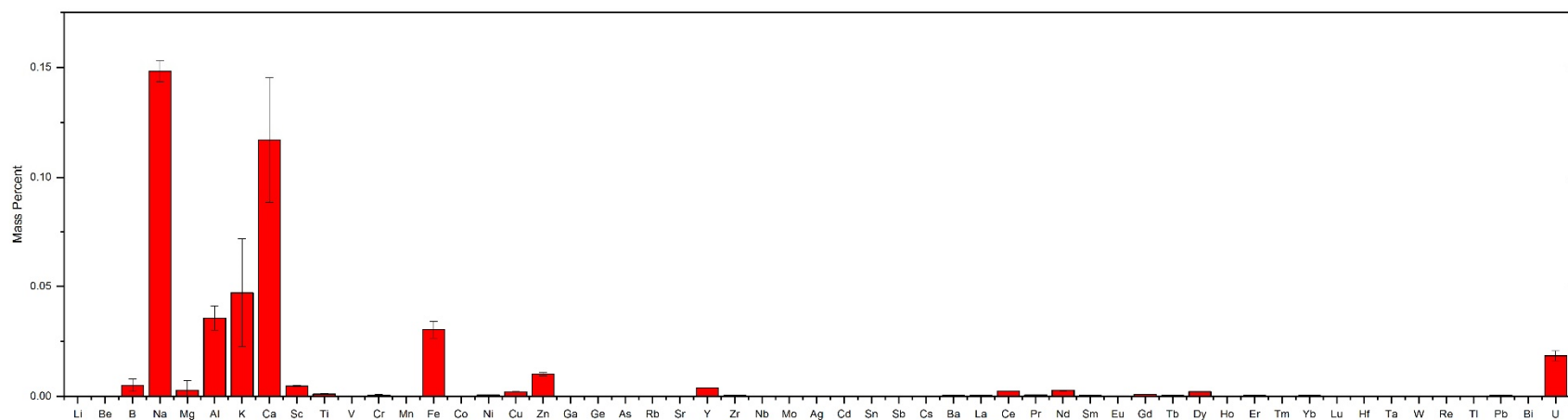


Fig. 4 Full mass spectrometry data for final product in conc. HNO₃ acid; balance is thorium (99.5 ± 1.2 wt. %). For simplified figure in text (Fig. 15) elements have been categorized as alkali metals (Li, Na, K, Rb, Cs), alkaline earth metals (Be, Mg, Ca, Sr, Ba), early transition metals (Sc, Ti, V, Cr, Mn, Y, Zr, Nb, Mo, Hf, Ta, W, Re), late transition metals (Fe, Co, Ni, Cu, Zn, Ag, Cd), lanthanides (La-Lu) and post transition metals (B, Al, Ga, Ge, As, Sn, Sb, Tl, Pb, Bi); for each group the total mass percent was calculated.

