

Supporting Information

An Insightful Study on the Reduction and Extraction of Neptunium Assisted by Molybdenum

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1. Experimental Section

1.1 Chemicals and materials

The stock solution of ^{237}Np and TRPO were provided by Institute of Nuclear and New Energy Technology (INET), Tsinghua University. $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$, MoCl_5 and other metal nitrates were purchased from Sigma-Aldrich Reagent Company. L-ascorbic acid was obtained from Aladdin Reagent Company and Milli-Q water was utilized for all the experiments. Unless otherwise specified, the purities of all the extra reagents used in this work were of analytical or higher grade. Particularly, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ and MoCl_5 were alleged as molybdenum source of Mo(VI) and Mo(V) ion for all the experiments. **CAUTION:** ^{237}Np is a highly toxic radionuclide. The emitted alpha particle will form inhalable radioactive aerosol and cause serious internal radiation hazards. All radioactive related operations thus must be carried out in specifically designed negative pressure facilities.

1.2 Measurements

The concentration of ^{237}Np in the solvent extraction and spectral analysis experiments were determined through the ultra-low background liquid scintillation spectrometer (Quantulus 1220, PerkinElmer). The concentrations of non-radioactive coexisting metal ions were measured by Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES, Thermo Elemental, Inc.). The absorption spectra and relative proportion of Np(IV)/Np(V) were determined by UV-Vis-NIR spectrophotometer (Cary 6000i, Agilent, Inc.). XPS spectra were obtained on an ESCALAB Xi+ X-ray photoelectron spectrometer (Thermo Fisher Scientific, Inc.).

1.3 Solvent extraction

The TRPO ligand dissolved in *n*-dodecane was the organic phase. The HNO_3 solution containing Np and different concentrations of AA and concomitant metal ions was the aqueous phase. In light of the extraction of HNO_3 by the neutral extractant TRPO, the organic phase was pre-equilibrated with the corresponding blank HNO_3 solution at least three times to ensure a constant acidity before and after extraction. Two extraction modes were involved in this work: independent mode and dependent mode. In the independent mode, the aqueous solution (1.0

mL) containing AA and Np(V) was firstly stirred individually in a stoppered glass test tube (Np(V) reduction) and then mingled with equal volume (1.0 mL) of TRPO/*n*-dodecane organic solution for a period (Np extraction). In the dependent mode, equal volumes (1.0 mL) of the aqueous phase and the organic phase were directly agitated for appropriate time (simultaneous Np(V) reduction and Np extraction). Afterwards, the mixed two phases were separated by centrifugation. 100 μ L solution was sampled from each phase with a pipette and injected into 10 mL plastic scintillation vials. 3 mL of scintillation cocktail (Hisafe 3) was added to the vial and mixed thoroughly. The samples were then analyzed on an ultra-low background liquid scintillation spectrometer. The distribution ratio (*D*) of ^{237}Np was defined as $D = [\text{Np}]_{\text{org.}}/[\text{Np}]_{\text{aq.}}$, where $[\text{Np}]_{\text{org.}}$ is the concentration of Np in the organic phase and $[\text{Np}]_{\text{aq.}}$ represents that of Np in the aqueous phase. Triplicate experiments were performed to ensure the reproducibility and accuracy of the extraction data.

1.4 Preparation of the blue precipitate

140 mM Mo(VI) (20 eq. of Mo content in HLLW) and 0.1 M AA were added into 1.0 M HNO_3 and stirred for 20 min. The fine blue solid particles were rapidly generated and aggregated to precipitate. The resulting precipitate was then filtered under reduced pressure and allowed to dry at room temperature for further analysis.

1.5 Absorption spectra collection

In a typical operation of absorption spectra collection, the sample solution containing Np or Mo was carefully added into a 10 mm screw-capped quartz cuvette. Reference solution was 1.0 M HNO_3 or 1.0 M TRPO/*n*-dodecane for the aqueous or organic samples, respectively. Spectra were collected in the wavelength range of 200-1400 nm. The temperature of the sample and reference solution was controlled using an external temperature controller and maintained as a constant of 25.0 ± 0.1 °C.

1.6 Incorporation of Np & Mo into the organic solvent

For the incorporation Np, 1.0 M TRPO/*n*-dodecane organic solution was mixed with equal volume of 1.0 M HNO_3 solution containing Np(IV) or Np(V) or Np(VI) for 20 min to obtain

the Np(IV) or Np(IV/V/VI) or Np(VI)-incorporated TRPO/*n*-dodecane organic solution.

For the incorporation Mo, 35 mM of Mo(VI) (5 eq. of Mo content in HLLW) and 0.1 M AA were firstly added in 1.0 M HNO₃ and stirred for 20 min. Subsequently, the aqueous solution was contacted with equal volume of 1.0 M TRPO/*n*-dodecane organic solution for 10 min. The mixture was then separated through centrifugation to obtain the MB-incorporated TRPO/*n*-dodecane organic solution. Similarly, another MB-incorporated TRPO/*n*-dodecane organic solution was prepared with initial Mo(VI) concentration of 140 mM (20 eq. of Mo content in HLLW) and such a MB-incorporated organic solution was continuously stirred for a period until the MB completely disintegrated in the organic solution, resulting in a Mo(V)-incorporated TRPO/*n*-dodecane organic solution.

2. Supplementary Figures (Figure S1 to Figure S10)

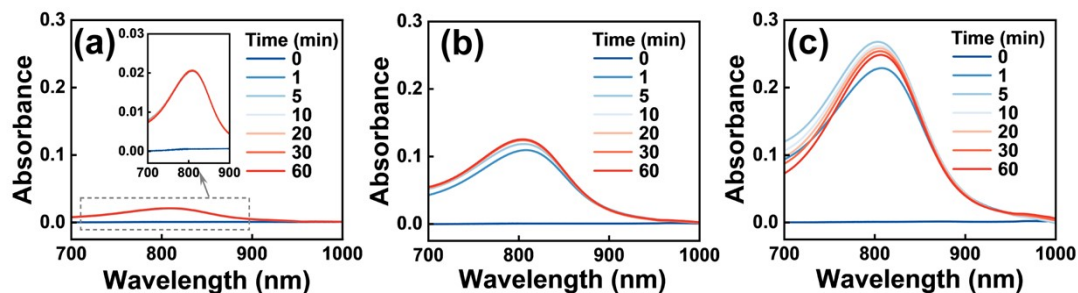


Figure S1. Time-dependent changes in the absorption spectra of AA-Mo(VI) mixture. Initial aqueous phase: 0.1 M AA and (a) 7 mM, (b) 35 mM, (c) 70 mM (1, 5, 10 eq.) Mo(VI) in 1.0 M HNO₃. Mixing time: 0-60 min. Temperature: 25.0 ± 0.1 °C.

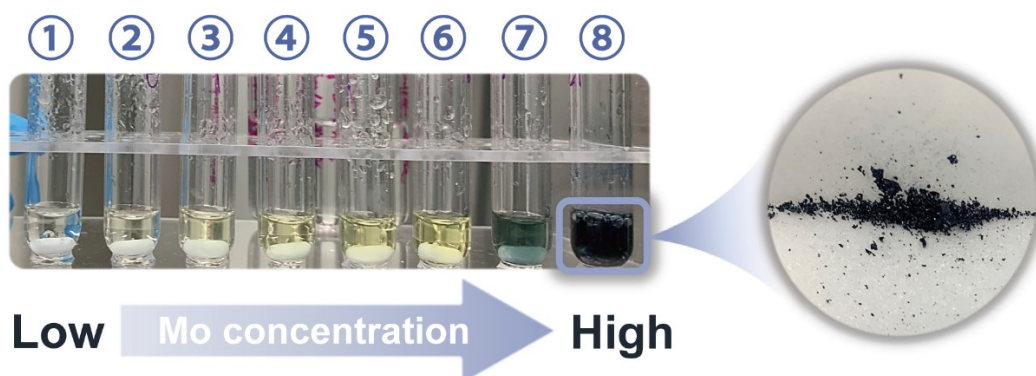


Figure S2. Images of AA mixing with different concentrations of Mo(VI). Initial aqueous phase: 0.1 M AA and (1) 1.4 mM, (2) 3.5 mM, (3) 7 mM, (4) 14 mM, (5) 35 mM, (6) 70 mM, (7) 105 mM, (8) 140 mM (0.2-20 eq.) Mo(VI) in 1.0 M HNO₃. Mixing time: 30 min. Temperature: 25.0 ± 0.1 °C.

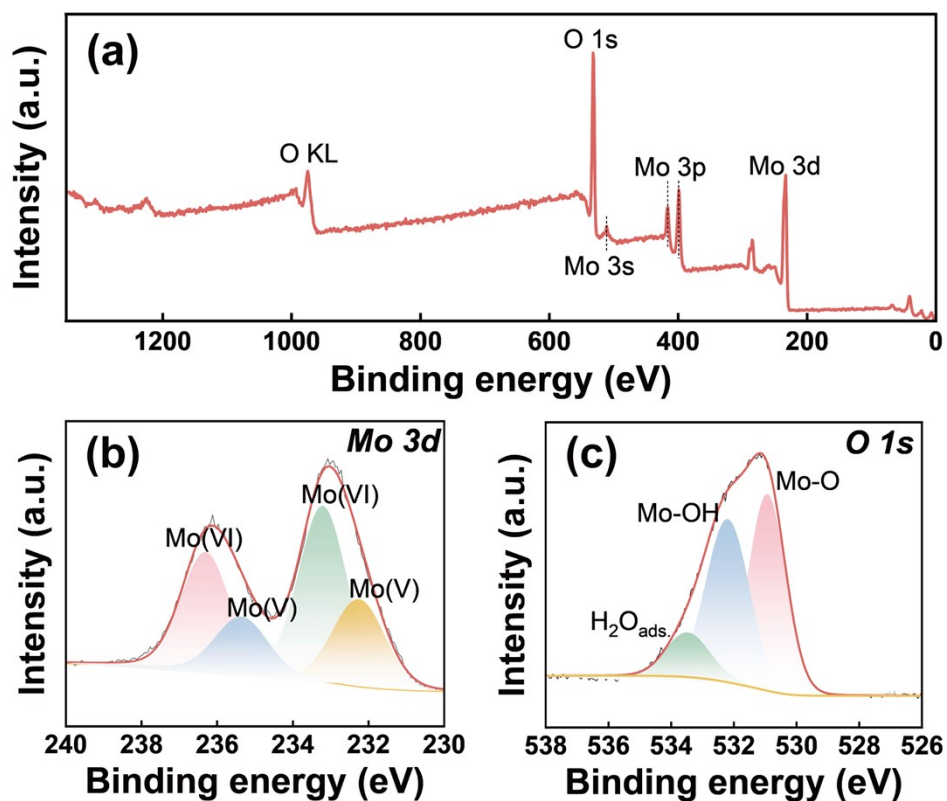


Figure S3. (a) The typical XPS survey spectrum of the blue precipitate. (b) High-resolution spectrum of Mo 3d. (c) High-resolution spectrum of O 1s.

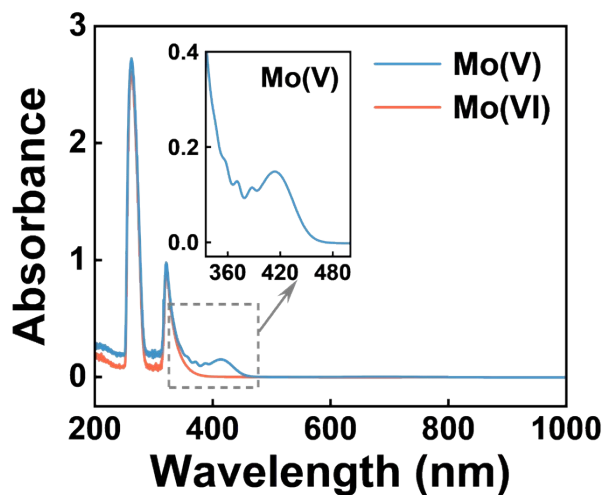


Figure S4. Absorption spectra of Mo(VI) and Mo(V) in 1.0 M HNO₃, respectively. (NH₄)₆Mo₇O₂₄·4H₂O and MoCl₅ were identified as molybdenum source of Mo(VI) and Mo(V). Temperature: 25.0 ± 0.1 °C.

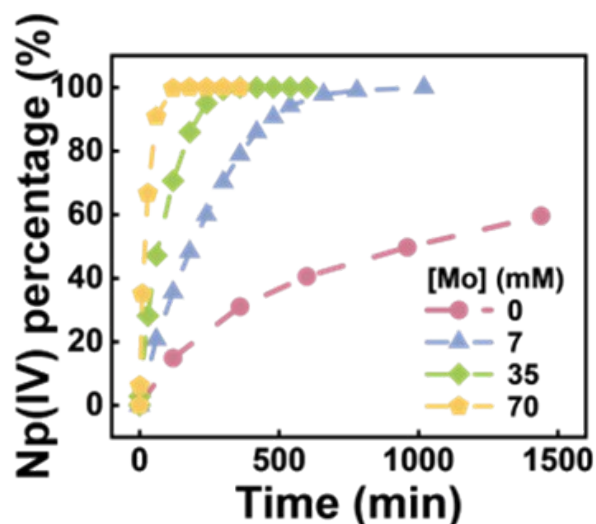


Figure S5. Time-dependent changes of percentages of Np(IV) with the presence of different concentrations of Mo(VI) in aqueous solution. Initial aqueous phase: 0.1 mM Np(V), 0.1 M AA and (a,b) 0 mM, (c,d) 7 mM, (e,f) 35 mM, (g,h) 70 mM (0, 1, 5 and 10 eq.) Mo(VI) in 1.0 M HNO₃. Mixing time: (a,b) 0-6360 min; (c,d) 0-1020 min; (e,f) 0-540 min; (g,h) 0-360 min. Temperature: 25.0 ± 0.1 °C.

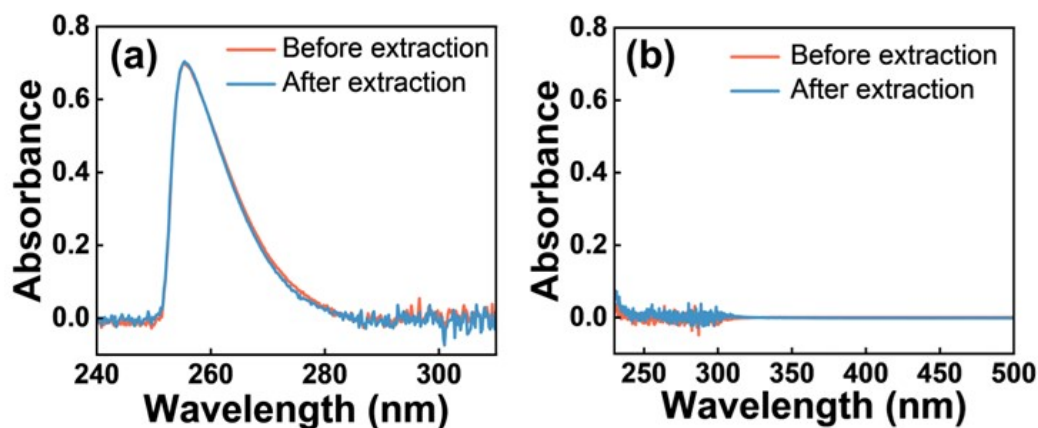


Figure S6. Absorption spectra of (a) the aqueous phase and (b) the organic phase before and after extraction of AA by TRPO. Initial aqueous phase: 0.1 M AA in 1.0 M HNO₃. Initial organic phase: 1.0 M TRPO/*n*-dodecane. Contact time: 30 min. Temperature: 25.0 ± 0.1 °C. The obtained samples of the aqueous phase and the organic phase were diluted 800 times and 5 times, respectively to ensure accurate measurement.

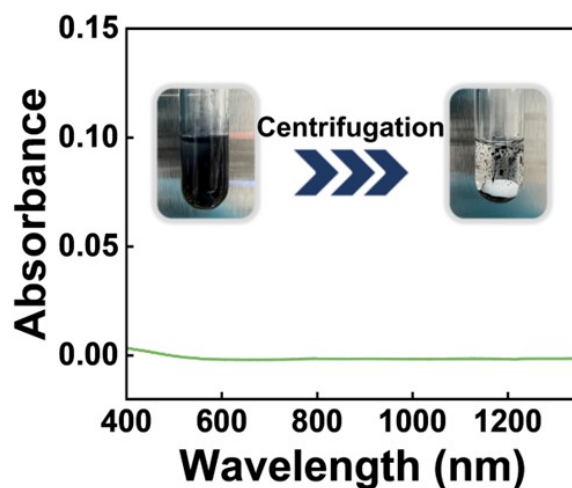


Figure S7. Absorption spectrum and images of *n*-dodecane after mixing with MB.

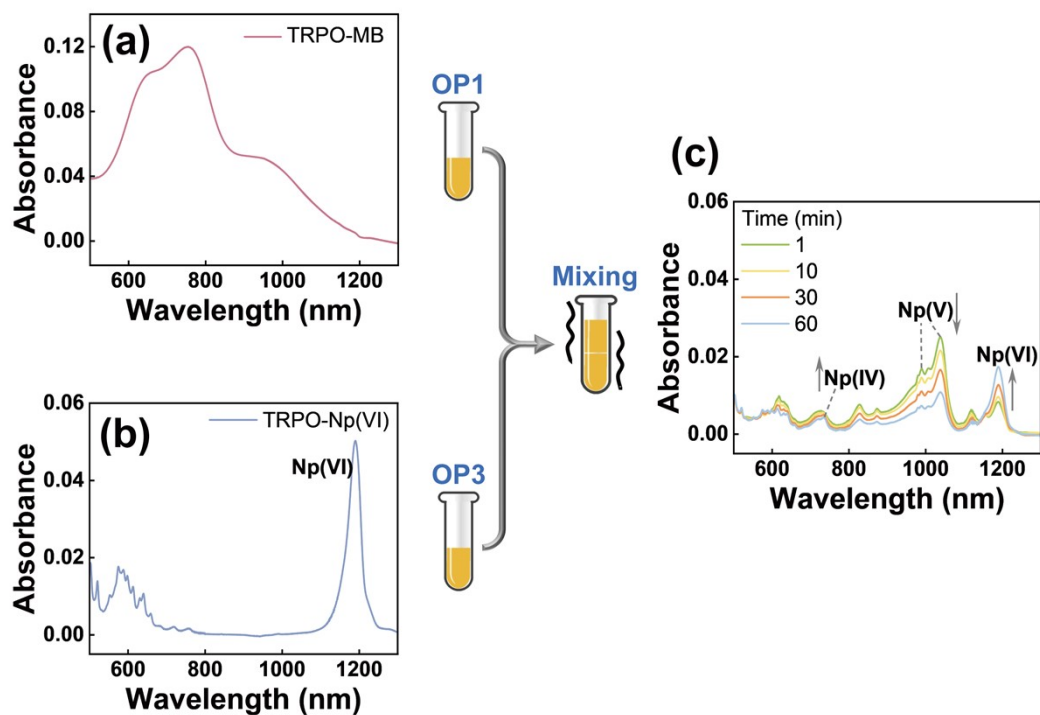


Figure S8. Absorption spectra of (a) MB-incorporated organic solution (OP1) and (b) Np(VI)-incorporated organic solution (OP3). (c) Time-dependent changes of absorption spectra of OP1 and OP3 mixture. Initial OP1: 0.8 mL of MB-incorporated 1.0 M TRPO/*n*-dodecane solution. Initial OP3: 0.8 mL of 1.08 mM Np(VI)-incorporated 1.0 M TRPO/*n*-dodecane solution. OP1 and OP3 were continuously mixed for 60 min and paused at 10, 30 and 60 min, respectively for spectra collection. Temperature: 25.0 ± 0.1 °C.

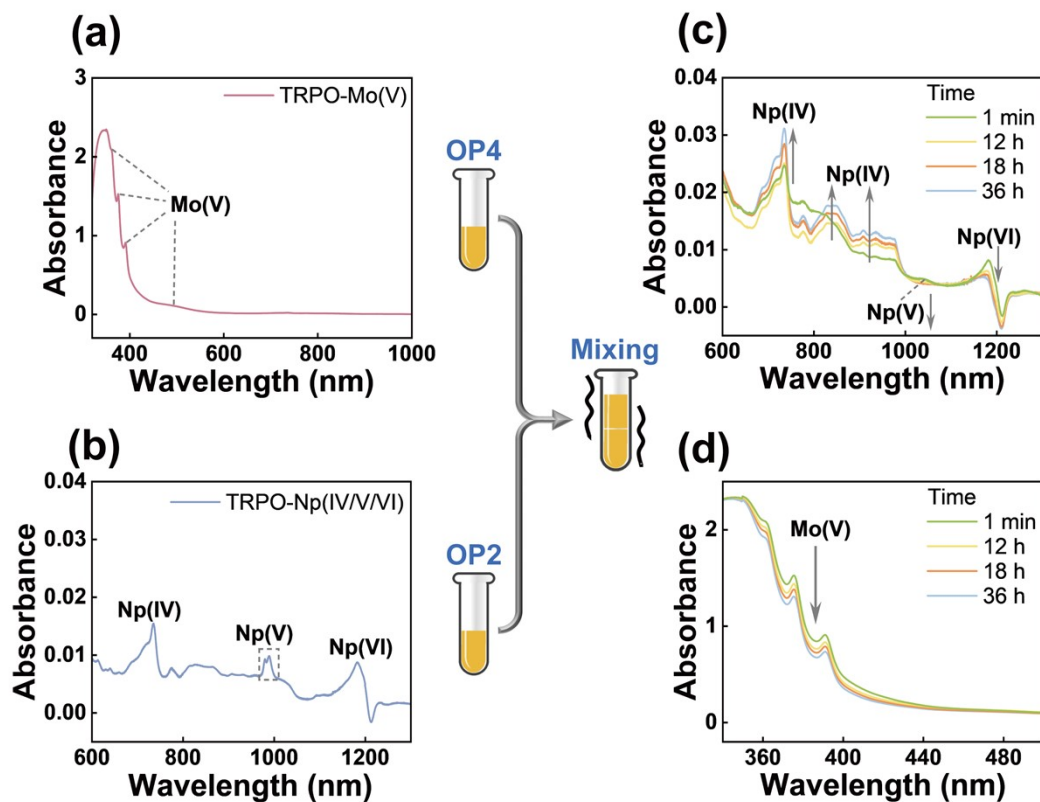


Figure S9. Absorption spectra of (a) Mo(V)-incorporated organic solution (OP4) and (b) Np(IV/V/VI)-incorporated organic solution (OP2). (c,d) Time-dependent changes of absorption spectra of OP4 and OP2 mixture. Initial OP4: 0.4 mL of Mo(V)-incorporated 1.0 M TRPO/*n*-dodecane solution. Initial OP2: 0.8 mL of 0.38 mM Np(IV/V/VI)-incorporated 1.0 M TRPO/*n*-dodecane solution. OP4 and OP2 were continuously mixed for 36 h and paused at 1 min, 12, 18 and 36 h, respectively for spectra collection. Temperature: 25.0 ± 0.1 °C.

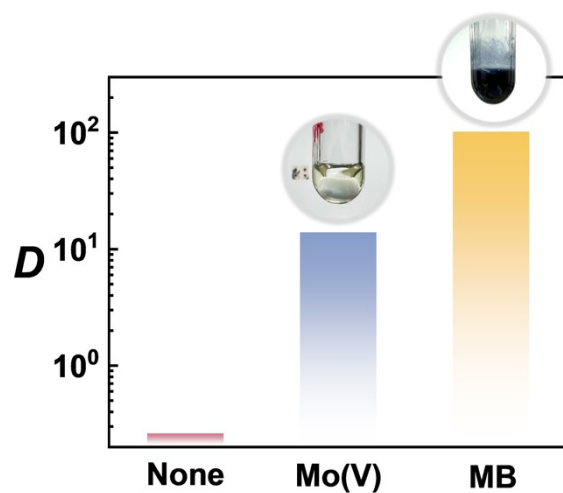


Figure S10. Effect of the absence/presence of Mo and the species of Mo on the extraction of Np by TRPO. Initial aqueous phase: 0.13 mM Np(V), 0.1 M AA and the absence/presence of Mo(V) or MB in 1.0 M HNO₃. Initial organic phase: 1.0 M TRPO/*n*-dodecane. The extraction was operated in the independent mode. Temperature: 25.0 ± 0.1 °C.

3. Supplementary Table

Table S1. Composition of simulated feed solution.

Element	Concentration (mM)	Element	Concentration (mM)
Ba	2.76	Ni	0.78
Cd	0.33	Pd	2.85
Ce	3.34	Pr	1.59
Cr	1.19	Rb	0.81
Cs	3.38	Rh	0.74
Eu	0.18	Ru	4.46
Fe	4.24	Sm	0.98
Gd	0.24	Sn	0.14
La	1.73	Sr	1.62
Mo	7.03	Te	0.75
Na	49.41	Y	1.00
Nd	5.55	Zr	7.85
Np	0.45		