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Extracting Performance of Cesium by 25,27-Bis(2-Propyloxy) Calix[4]-26,28-Crown-6 (iPr-C[4]C-6) in n-octanol

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Abstract: In this work, the extraction of cesium(Cs^+) in nitric acid and in a simulated high level liquid waste (HLLW) by iPr-C[4]C-6 was investigated in the diluent n-octanol. The slope of the extractant dependency equals 1, indicating that the complex has $1:1[Cs^+ \cdot \text{iPr-C[4]C-6}]Cs^+$ to ligand. 0.025 mol/L iPr-C[4]C-6 in n-octanol (abbreviated to iPr-C[4]C-6-n-octanol) has a stronger extracting ability to Cs when acidities are between 1.0 mol/L and 4.0 mol/L. The stripping properties of Cs loading in 0.025 mol/L iPr-C[4]C-6-n-octanol was studied. Cs loading in iPr-C[4]C-6-n-octanol can be stripped easily into the aqueous phase because the distribution ratios of Cs are lower than 0.5 when pH is between 2 and 10 in the aqueous phase. On the above basis, the better parameters were selected and the cold cascade test for removing Cs from the simulated HLLW was investigated on miniature centrifugal contactor. The results of the test are attractive. The removing ratio of Cs from the simulated HLLW is 99.5% and the stripping ratio of Cs loading in 0.025 mol/L iPr-C[4]C-6-n-octanol is 99.2%. The results show that 0.025 mol/L iPr-C[4]C-6-n-octanol is an effective process for removing Cs from HLLW.

Keywords: Extraction, cesium, calixcrown, HLLW

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INTRODUCTION

The treatment and disposal of HLLW is a subject of great public concern. The most possible method is to vitrify HLLW into borosilicate glass matrix and then dispose it in a deep repository, but it makes the volume of glass larger. If the actinides and long-life fission elements are removed and vitrified, the vitrified waste volume will be reduced. ^{90}Sr and ^{137}Cs are two key elements in long-life fission product besides actinides. There are good solvent extraction methods to remove actinides (1, 2) and ^{90}Sr (3–5) from HLLW, but there are not good extraction methods to remove ^{137}Cs from HLLW. The calixcrown is the most promising extractant and the scientists in the world are investigating it to extract ^{137}Cs from HLLW (6–9). But there are two key problems to be solved. One problem is the larger scale synthesis of calixcrown for industry application. Another one is to select good diluents. Some scientists have selected some good diluents and these diluents were some mixing agents (10–12). In our laboratory, researchers investigated well the synthesis of 25,27-Bis(2-propyloxy) calix[4]-26,28-crown-6(iPr-C[4]C-6) (13) and selected n-octanol as the diluent (14, 15).

In this paper, the extraction properties of Cs by 0.025 mol/L iPr-C[4]C-6-n-octanol was investigated and a cold cascade test was carried out for removing Cs from a simulated Chinese HLLW by 0.025 mol/L iPr-C[4]C-6-n-octanol.

EXPERIMENTAL

Instrumentation

Miniature Centrifugal contactor set was made in INET, Tsinghua University. The rotor diameter was 10 mm, and its hold-up volume was about 3–4 mL in each stage. It is convenient by using miniature centrifugal contactor to research extraction technology, especially the cascade test (16). Pumps: All feed solutions in the cold cascade test were pumped by miniature gear pumps, made by Prominent Fluid Controls Corporation, Germany.

Agent

25,27-Bis(2-propyloxy) calix[4]-26,28-crown-6(iPr-C[4]C-6) synthesized by INET, Tsinghua University. Its purity is more than 99.5%.

The 0.025 mol/L iPr-C[4]C-6-n-octanol is prepared as following: iPr-C[4]C-6 is diluted by heating n-octanol to 40–50°C and cools the solution to the room temperature. The solution is stable when the temperature is higher than 5°C. Other agents are analytical grade.

The main composition of a simulated Chinese HLLW is listed in Table 1.

Table 1. The main composition of a simulated Chinese HLLW

Element	Cs	Na	K	Sr	Al	Fe	Cr	Ni	Mo	Nd
Concentration/g/l	0.93	16.5	0.15	0.24	5.21	6.45	0.62	3.43	0.32	1.74

Analytical Methods

Cs was determined by atomic absorption spectrophotometer (Hitachi 180-80, Japan) and other elements were determined by ICP-AES (IRIS Advantage, TJA Solution, USA). ^{137}Cs activity was detected with a Ge-Li detector (EG&G, UAS). The concentration of HNO_3 in aqueous phase was determined by caustic titration. The concentration of HNO_3 in organic phase was first stripped into an aqueous phase and then determined by caustic titration.

Extraction Process

Prior to measuring distributions, extractant (different concentration iPr-C[4]C-6 in n-octanol) was pre-equilibrated with different HNO_3 concentration by contacting 3–4 times for 10 minutes each time in equal volume. The pre-equilibrated organic phase was mixed with equal volume of the simulated HLLW or solution containing elements for 10 minutes. The two phases were centrifuged and separated for analysis. The distribution ratio of M element was calculated by $D_M = [X]_o/[Y]_A$, where $[X]_o$ and $[Y]_A$ are equilibrium concentration of elements in organic and aqueous phase, respectively. The tests were carried out at room temperature ($25 \pm 0.1^\circ C$). The separation factor of M element to Cs was calculated by S. F. = D_{Cs}/D_M.

Stripping Process

Cs loading in 0.025 mol/L iPr-C[4]C-6-n-octanol was stripped five times by using pH = 2 HNO_3 fresh solution each times. The stripping ratio is calculated by the following equation: Stripping ratio $= (1 - C_i/C_0) \times 100\%$, where C_i is the concentration of Cs remained in organic phase after the i times stripping by pH = 2 HNO_3 fresh solution; C_0 is the original concentration of Cs in organic phase.

The Cold Cascade Test Process

The cold cascade test for removing Cs from a simulated HLLW (The main composition of the HLLW is listed in Table 1) was carried out on the miniature centrifugal contactor and the flow sheet and process parameters are presented in Table 2 and Fig. 1. In the extraction section, 2 scrubbing

Table 2. The parameters of the process

Process	Composition	Flow rate (mL/h)
1AF	HNO_3: 1.0 mol/L, the composition is listed in Table 1	78
1AX	0.025 mol/L iPr-C[4]C-6-n-octanol	67
1AS	0.5 mol/L HNO_3	36
1AW	The raffinate	114
1BX	0.005 mol/L HNO_3	70

stages were selected to scrub K and Mo extracted in 0.025 mol/L iPr-C[4]C-6-n-octanol and to scrub the aqueous carryover in organic phase.

The cold cascade test was carried out in the following steps: first the miniature centrifugal contactor was filled with 1AS, 1BS aqueous solution by gear pumps, and then the organic phase was pumped. 1AF feed solution was pumped when organic phase had flowed out of the contactor set and the cold cascade test began. The extraction system reached the equilibrium state when the all outlet acidities were not changed and run for one hour again. And then all pumps and contactor set were stopped and both phases remaining in each stage of contactor set were collected for analysis.

RESULTS AND DISCUSSION

The Relation Between the Concentration of iPr-C[4]C-6-n-Octanol and D_{Cs}

The relation between the concentration of iPr-C[4]C-6-n-octanol and D_{Cs} was investigated and is shown in Fig. 2. Tracing ^{137}Cs was used to keep lower Cs concentration for investigating the relation. Figure 2 shows that the extractant dependencies exhibit a slope of approximately 1. It indicates the complex of iPr-C[4]C-6 with Cs is as follows: iPr-C[4]C-6:Cs and final species is [iPr-C[4]C-6:Cs]NO_3 according to the electric neutral rule.

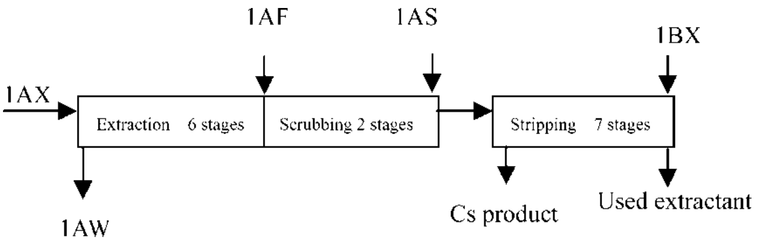

Figure 1. The flow sheet of cold cascade test.

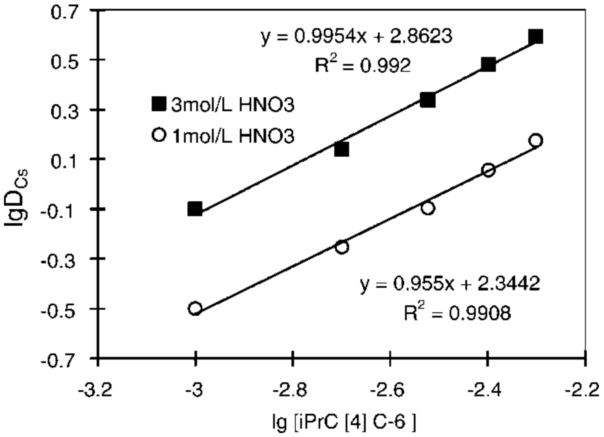

Figure 2. The effect of iPr-C[4]C-6 concentration in n-octanol on D_{Cs}.

The Effect of HNO_3 Concentration in Aqueous Phase on D_{Cs}

The organic phase is 0.025 mol/L iPr-C[4]C-6-n-octanol and the aqueous phase is the solution containing different concentration of HNO_3 and initial Cs. The results are shown in Fig. 3. The data in Fig. 3 shows that D_{Cs} is increased with the increasing of HNO_3 concentration when the HNO_3 concentration is between 0.001 to 3 mol/L. But D_{Cs} is decreased with the increasing of HNO_3 concentration when HNO_3 concentration is more than 3 mol/L. The reason is that the salt-out effect is obvious when HNO_3 concentration is lower, but the competition between HNO_3 and Cs lead the D_{Cs} to decrease when the content of HNO_3 extracted by iPr-C[4]C-6 is increased in higher HNO_3 concentration. D_{Cs} is changed little in simulated HLLW with the increasing of

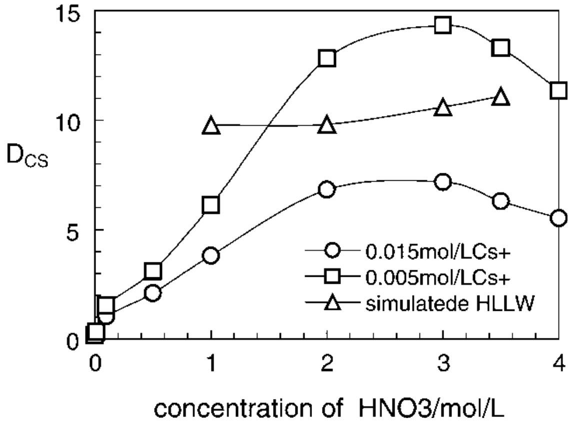

Figure 3. The effect of HNO_3 concentration on D_{Cs}.

HNO_3 concentration because the salt-out effect is very obvious for higher salt in the simulated HLLW. Figure 3 also shows that D_{Cs} is decreased with the concentration of Cs, but D_{Cs} is higher, more than 5 when the concentration of HNO_3 is about 2.5 mol/L.

Effect of Cs Concentration in Aqueous Phase on D_{Cs}

The effect of Cs concentration on D_{Cs} was studied under the following condition: The concentration of iPr-C[4]C-6 is 0.025 mol/L and deferent initial concentrations of Cs are changed from 0.001 to 0.03 mol/L. Figure 4 shows that D_{Cs} is decreased with the increasing of Cs concentration. D_{Cs} is decreased sharply when the Cs concentration is equal to or larger than the concentration of iPr-C[4]C-6. The reason is that the complex of iPr-C[4]C-6 with Cs is formed 1 : 1 species and the free iPr-C[4]C-6 is lower when content of Cs near or equal to the concentration of iPr-C[4]C-6 is extracted by iPr-C[4]C-6. The concentration of iPr-C[4]C-6 could be chosen in treating HLLW according to the Cs concentration.

Stripping Properties of Cs Loading in 0.025 mol/L iPr-C[4]C-6 in n-octanol

In order to investigate the stripping properties of Cs, D_{Cs} in different pH of HNO_3 solution was studied by using 0.025 mol/L iPr-C[4]C-6-n-octanol. The results are presented in Fig. 5. Figure 5 shows that D_{Cs} is deceased with the increasing of pH when pH is between 0.5 and 4, and increased a little when pH is more than 4. D_{Cs} is lower than 1 when pH was between 2 to 10, so nitric solutions of pH = 2 to 10 are selected as the stripping solution.

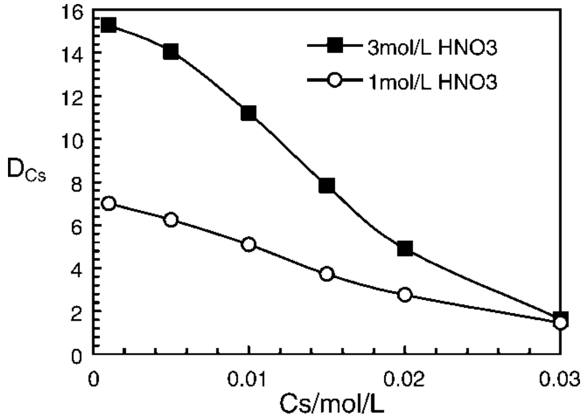

Figure 4. Effect of Cs concentration in aqueous phase on D_{Cs}

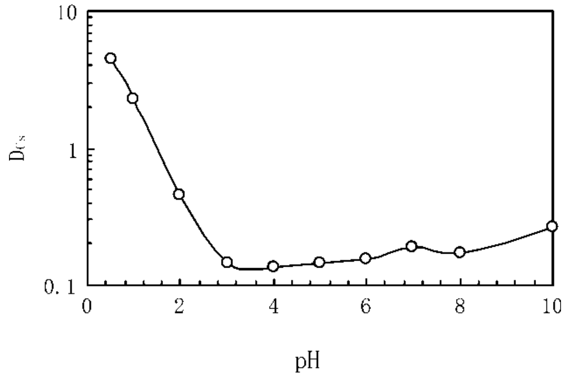

Figure 5. Effect of pH on D_{Cs}.

The five times stripping properties of Cs loading in 0.025 mol/L iPr-C[4]C-6-n-octanol were studied by using fresh pH = 2 HNO_3 solution. The results are listed in Table 3 and show that 99.7% (stripping ratio of Cs) is obtained by stripping five times. The stripping ratio of Cs can be ensured by using pH = 2 to 10 HNO_3 solution according to the results.

The Extraction Abilities of 0.025 mol/L iPr-C[4]C-6 -n-octanol to Some Elements

In order to investigate the extraction ability to some elements in simulated HLLW, the distribution ratios of these elements were studied in the simulated HLLW composed in Table 1 and then calculated their separation factors to Cs. The conditions of test are as followed: 0.025 mol/L iPr-C[4]C-6-n-octanol, HNO_3: 1.0 mol/L. The results are listed in Table 4. Table 4 shows that 0.025 mol/L iPr-C[4]C-6-n-octanol has much weaker extraction abilities to some elements, such as Al, Fe, Ni, Cr, Nd, Sr, Na and their D_M were lower than 10^{-3} and value of S.F. for Na was 978, other element's were larger than 3000.

0.025 mol/L iPr-C[4]C-6-n-octanol has a little extraction abilities to K, Mo, but D_M was lower than 0.2 and values of S.F. for K, Mo are 65.2, 75.2 respectively. D_{Cs} is about 9.78, much larger than that of other elements. The results indicate that the system composing of 0.025 mol/L iPr-C[4]C-6-n-octanol has a stronger selectivity and extraction ability to Cs.

Table 3. The stripping properties of Cs loading in iPr-C[4]C-6 in n-octanol

Times of stripping	1	2	3	4	5
Stripping ration/%	63.1	89.3	97.1	98.6	99.7

Table 4. Extracting abilities to some elements in simulated HLLW

Elements	g/L	D	S.F.
Al^{3+}	5.21	8.9E-04	1.1E + 04
Cr^{3+}	0.62	1.4E-03	7.0E + 03
Fe^{3+}	6.45	1.8E-03	5.4E + 03
K^{+}	0.15	1.5E-01	65.2
MoO_4^{2-}	0.321	1.3E-01	75.2
Na^{+}	16.5	1.0E-02	978.0
Nd^{3+}	1.74	1.3E-03	7.5E + 03
Ni^{2+}	3.37	2.4E-03	4.1E + 03
Sr^{2+}	0.24	2.9E-04	3.3E + 03
Cs^{+}	0.93	9.78	1.0

The Cold Cascade Test for Simulated HLLW on the Miniature Centrifugal Contactor

The parameter of the cold cascade test was selected and is listed in Table 2 and Fig. 1 according to the extraction ability of 0.025 mol/L iPr-C[4]C-6-n-octanol to Cs in the simulated HLLW. 0.005 mol/L HNO_3 solution was selected as the stripping solution according to D_{Cs} in HNO_3 solution and stripping properties of Cs loading in 0.025 mol/L iPr-C[4]C-6-n-octanol.

The concentration profiles of HNO_3 and Cs are shown in Figs 6–7 and D_{Cs} at each stage is listed in Table 5. The results show that the concentration of HNO_3 is stable in extraction section, but sharply decreased in the scrubbing section. At the same time, D_{Cs} is between 2.5 and 8.7 in extraction section. The removing ratio of Cs from the simulated HLLW is 99.5% by calculating the concentration of Cs in the raffinate and feed solution. D_{Cs} is about 7 in the scrubbing section to prevent the accumulation of Cs. The concentration of HNO_3 is about 0.1 mol/L at the first stage of the stripping section and

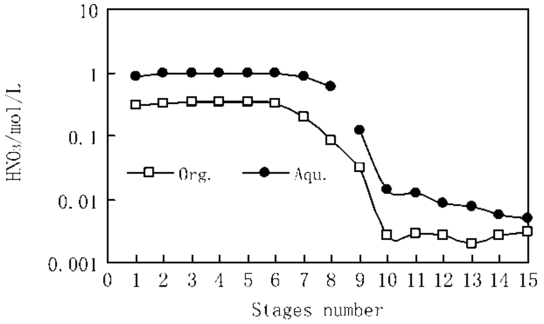

Figure 6. The distribution of HNO_3 in aqueous and organic phase at each stage.

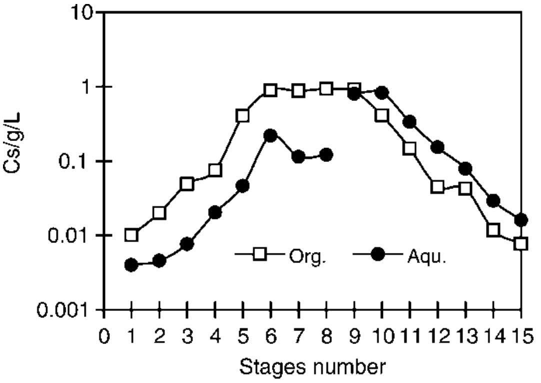

Figure 7. The distribution of Cs in aqueous and organic phase at each stage.

D_{Cs} at the first stage is near 1. But D_{Cs} at other stages is about 0.4, and it could ensure the stripping ratio of Cs by 7 stripping stages. The stripping ratio of Cs is 99.2%. The much better results of stripping ratio will be gotten if the HNO_3 concentration of the scrubbing solution is changed much lower to decrease the concentration of HNO_3 of the organic phase in scrubbing section and the stripping solution, 0.005 mol/L HNO_3 is changed into between 10^{-3} mol/L and 10^{-6} mol/L. Not only can it keep from accumulation of Cs for the lower D_{Cs} in the scrubbing section, but also Cs in the organic phase can be stripped well because D_{Cs} is much lower for the lower HNO_3 concentration of the organic phase in the scrubbing section and the stripping section.

Table 5. The distribution ratio of Cs at each stage

Stages	D_{Cs}
1	2.5
2	4.4
3	6.4
4	3.7
5	8.7
6	4.1
7	7.7
8	7.7
9	1.1
10	0.5
11	0.4
12	0.3
13	0.5
14	0.4
15	0.4

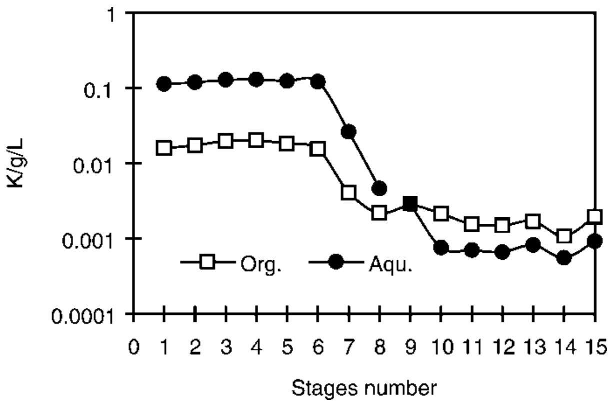

Figure 8. The distribution of K in aqueous and organic phase at each stage.

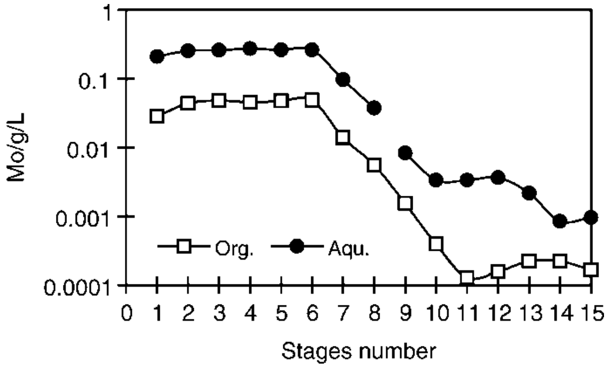

Figure 9. The distribution of Mo in aqueous and organic phase at each stage.

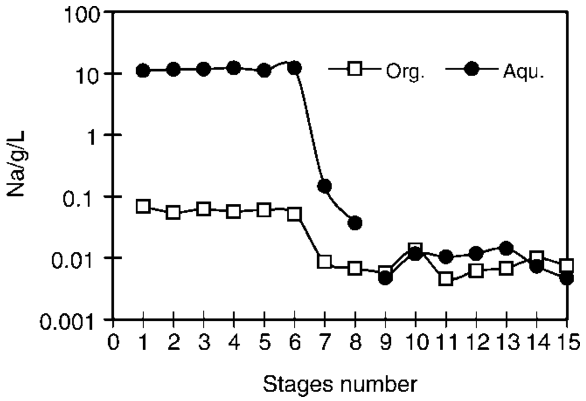

Figure 10. The distribution of Na in aqueous and organic phase at each stage.

Table 6. The distribution of some elements in each flow and material balance

Element	Raffinate	Cs product	Used extractant	Material balance
	Distribution %			
Cs	0.86	98.62	0.52	89.5
Na	99.98	0.01	0.01	108
K	99.29	0.39	0.32	108
Sr	99.54	0.26	0.20	103
Al	100.00	—[a]	—	106
Fe	99.99	0.00	0.01	111
Cr	100.00	—	—	103
Ni	99.98	0.02	—	102
Mo	98.73	1.18	0.09	108
Nd	99.98	—	0.02	106

[a]— No detected.

Concentration profiles of other elements at each stage are shown in Figs. 8–10. The results show that D_M is much lower. Most of K, Mo and Na extracted into organic phase in extraction section could be scrubbed down into the aqueous phase by two-stages of scrubbing.

The distribution of some elements in each flow and material balance are calculated and listed in Table 6 according to the element concentrations in each flow. Table 6 shows that the material balance of elements is good, between 89.5 % and 111%. There are fewer other elements in Cs product and the retention of elements in the used organic phase is lower. The results indicates that 0.025 mol/L iPr-C[4]C-6-n-octanol has a good selectivity and extraction ability to Cs.

CONCLUSION

The complexant of iPrC[4]C-6 with Cs is formed 1:1. iPr-C[4]C-6-n-octanol has a good extraction ability and selectivity to Cs. Lager D_{Cs} was gotten by iPr-C[4]C-6-n-octanol in the simulated HLLW and Cs loading iPr-C[4]C-6-n-octanol was stripped well by 0.005 mol/L HNO_3. The results of the cold cascade test on the miniature centrifugal contactor are attractive for removing Cs from the simulated HLLW. 99.5% Cs in the simulated HLLW was removed and 99.2% Cs loading in iPr-C[4]C-6-n-octanol was stripped by 6 stages extraction, 2 stages scrubbing and 7 stages stripping. The results show that 0.025 mol/L iPr-C[4]C-6-n-octanol is an effective process for removing Cs from simulated HLLW. The further work need do, such as, the irradiated stability of iPr-C[4]C-6-n-octanol, the further optimization of extraction parameters for this process and the test of true HLLW.

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