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Cs^+ Extraction from Chloride-Rich Brine Solutions Using the Calixarene Crown Ether MAXCalix

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ABSTRACT

We have developed an extraction method for the retrieval of Cs^+ from chloridecontaining salt brine solutions. We employ the calixarene crown ether known as MAXCalix as the extractant, which exhibits a remarkable selectivity for Cs^+ over Na^+, K^+, Mg^{2+} and Ca^{2+}, with separation factors ranging from 100 to 10^4. The efficiency of the extraction strongly depends on the chloride concentration in the aqueous phase. Notably, when the chloride concentration reaches 4 mol L^{-1}, we achieve a Cs^+ distribution ratio of 7.9. Accordingly, the retrieval of Cs^+ from the organic phase is achieved when the HCl concentration is maintained at a low level. In multicomponent chloride brine solutions, the distribution ratios for Cs^+ are somewhat lower, yet still fall within the range of 4–6. Nevertheless, these ratios remain favorable for separation purposes. Additionally, the distribution ratios of Na^+, K^+, Mg^{2+}, and Ca^{2+} offer insights into the coordination chemistry of MAXCalix. Our experimental data indicate a correlation between ionic size and distribution ratio. Cs^+ forms the strongest complex, followed by K^+ and Na^+, while Mg^{2+} and Ca^{2+} exhibit minimal extraction, potentially due to interactions with the diluent. These findings may open new approaches for the development of a decontamination strategy tailored to address salts and brine solutions contaminated with Cs-137.

KEYWORDS
Calixarene crown ether; cesium separation; chloride; liquid-liquid extraction

Introduction

A large variety of elements across the periodic table are produced during the nuclear fission process of uranium and plutonium.[1–3] One of the most prominent fission products is Cs-137 ($t_{1/2} = 30.2$ a). Since Cs-137 is a beta emitting radionuclide and moreover Cs^+ is chemically related to the biological important ions Na^+ and K^+, an accidental release of this radionuclide may have a significant impact. It is estimated that about 10^{16} Bq Cs-137 has been released into the surrounding area during the Fukushima-daichi incident (2011).[4,5] In addition, Cs-137 might be present in significant quantities in low to intermediate level

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nuclear waste repositories during initial operational phases, including potential deep underground host rock formations like salt mines. Developing options for effective decontamination strategies targeting concentrated chloride brine media is potentially relevant in this context. The recovery of Cs^+, however, is challenging due to the chemical similarity of Cs^+ to Na^+ and K^+ - which are abundant in high quantities far exceeding Cs-137 concentrations and therefore, requires highly selective reagents and methods.

A potential method for cesium recovery is liquid-liquid extraction. Cs^+ separation has already been investigated in the context of nuclear fuel reprocessing using chlorinated cobalt dicarbolides,[6] crown ethers[7,8] or calixarene crown ethers[9–14] and other techniques.[15–17] In this context the most promising extracting agents are the calix-arene crown ethers BOBCalix[18–21] and MAXCalix[19,22] (structures see Figure 1). A common feature of these processes is the extraction of Cs^+ from nitrate-containing solutions. With regard of the application in a natural environment, the extraction has to be carried out from chloride-containing solutions. Recently published preliminary studies have shown that MAXCalix is a suitable extractant for this task.[23]

In this study, we present an extraction scheme for Cs-137 from chloride media using liquid-liquid extraction. Our focus relies on the Cs^+ extraction in presence of Na^+, K^+, Mg^{2+} and Ca^{2+} using the calixarene crown ether MAXCalix dissolved in a 1-octanol/kerosene diluent.

Material and methods

MAXCalix has been obtained from Marshallton Research Laboratories, King, North Carolina, USA. Metal salts and diluents have been purchased from Sigma Aldrich, Merck, and Alfa Aesar. For aqueous solutions MilliQ-water (Millipore, 18.2 MΩcm) has been used.

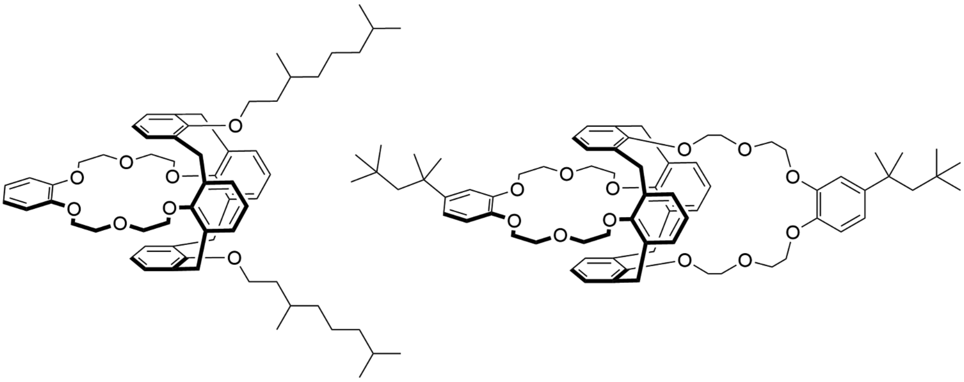

Figure 1. Structures of the calixarene crown ethers MAXCalix (left) and BOBCalix (right).

Distribution ratios were determined using a γ-counter (Packard Cobra Auto-Gamma 5003) with maximum acquisition time of 60 minutes and 0.3% deviation (500–680 keV for Cs-137 and 433–1417 keV for Na-22).

Na^+, K^+, Ca^{2+} and Mg^{2+} concentrations were determined by using ICP-OES (Optima 8300, Perkin Elmer). Cs^+ concentration was determined by F-AES (PinAAcle 500, PerkinElmer).

Experimental pH values were converted into the molal proton concentration pH_m ($pH_m = -\log m(H^+)$) at high ionic strength as described in the literature.[24]

Sample preparation

Extraction experiments with Cs-137 or Na-22 radiotracers

The organic and aqueous phase (500 µL each, ratio 1:1) were put into a 2 mL screw-cap glass vial. The aqueous phase was initially spiked with 10 µL radiotracer stock solution, resulting in a radionuclide concentration of 4 kBq mL^{-1} for Cs-137 and 1.64 kBq mL^{-1} for Na-22, respectively. The samples were shaken for 30 minutes at 20°C at 2500 rpm and in the following centrifuged for 2 min at 6000 rpm. Then 300 µL of each phase were separated and collected in γ-tubes. Cs-137 and Na-22 distribution ratios were determined by gamma counting.

Extraction experiments without radiotracer

The organic and aqueous phase (500 µL each, ratio 1:1) were put into a 2 mL screw-cap glass vial. The samples were shaken for 30 minutes at 20°C at 2500 rpm and in the following centrifuged for 2 min at 6000 rpm.

The phases were then prepared for ICP-OES or F-AES analytics as follows: 100 µL from the aqueous phase were separated and diluted to 1:100 ratio using suprapure 2% HNO_3. 300 µL of the separated organic phase and 3 mL 0.001 mol L^{-1} HCl were shaken for 30 minutes at 2500 rpm and then centrifuged for another 2 minutes at 6000 rpm. 1 mL of the resulting aqueous phase were separated and diluted to 1:10 ratio with 3% HNO_3.

In general, the distribution ratio is determined as follows.

$$D_M = \frac{\left[M_{org.phase}\right]}{\left[M_{aq.phase}\right]}$$

Distribution ratios are reproducible within an error range of approximately 10%.[25]

Results and discussion

A screening study showed that Cs^+ recovery from brine solutions is possible using calix-arene-crown ether ligands.[23] One of the commercially available ligands in that study, MAXCalix, has shown a reasonable selectivity for Cs^+ over Na^+, K^+ and other ions. Therefore, MAXCalix has been recommended for more detailed investigations regarding the development of an extraction process. Since our goal is to contribute to developing an extraction process scheme for the separation of radioactive cesium from brine solutions, all the relevant extraction parameters were studied systematically and were optimized.

Diluent choice

To reduce secondary waste generation, diluents and extractants composed of only C, H, O and N atoms are preferred. Accordingly, we studied the Cs^+ extraction using a 1-octanol/kerosene diluent. Figure 2 depicts D_{Cs} as a function of the kerosene volume fraction (w(kerosene). The highest D_{Cs} are achieved in pure 1-octanol with $D_{Cs} = 15.5$. Adding kerosene up to $60\%_v$ leads to a linear decrease of D_{Cs}. At higher kerosene contents $>80\%_v$, D_{Cs} declines drastically. In pure kerosene, we observe a D_{Cs} value of 10^{-3}, leading

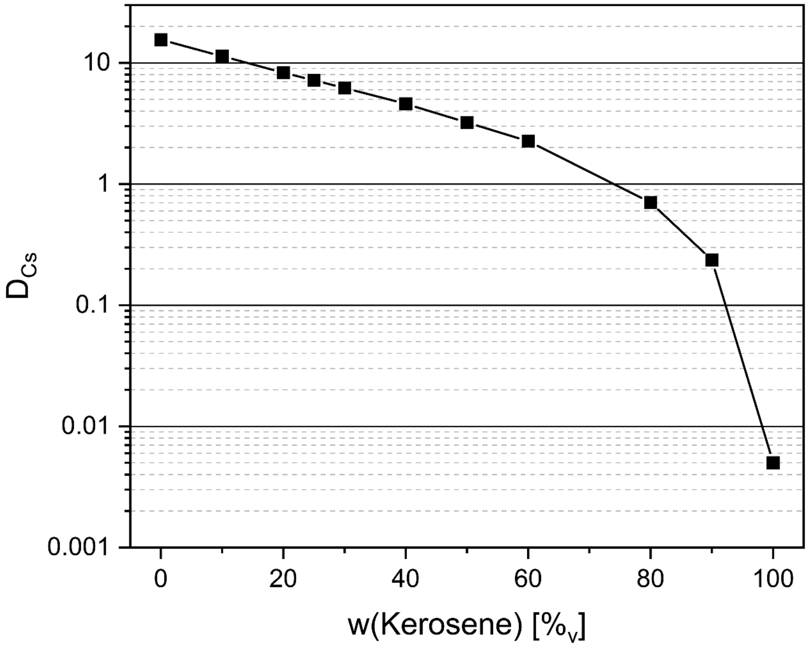

Figure 2. Cs^+ distribution ratios as a function of the kerosene volume fraction (w(kerosene) in % of the 1-octanol/kerosene mixture. Org. phase: 1-octanol/kerosene variable mixture, [MAXCalix] = 0.05 mol L^{-1}. Aq. phase: [Cs-133] = 10^{-4} mol L^{-1}, [Cs-137] = 4 kBq mL^{-1}, [NaCl] = 4 mol L^{-1}, [HNO_3] = 10^{-5} mol L^{-1}, $pH_m = 3$. A/O 1:1.

to four orders of magnitude difference in D_{Cs} compared to the pure 1-octanol system.

Thus, with a solvent comprising 0.05 mol L^{-1} MAXCalix, useful Cs^+ distribution ratios (i. e., $D_{Cs} > 1$) are obtained for kerosene volume fractions $<70\%_v$. As a compromise between decreasing distribution ratios and increasing solubility of MAXCalix (maximum solubility ≈0.05 mol L^{-1} in 1-octanol, ≈0.1 mol L^{-1} in kerosene) with increasing kerosene volume fraction, a $75/25\%_v$ 1-octanol/kerosene mixture was used as the diluent in all further experiments.

Extracting agent concentration

To find an optimal extracting agent concentration for the extraction process the distribution ratios of Cs^+ were acquired as a function of the MAXCalix concentration. The results are displayed in Figure 3. The D_{Cs} values increase from 2.6 ([MAXCalix] = 0.02 mol L^{-1}) to 11 ([MAXCalix] = 0.1 mol L^{-1}) almost linearly. The observed curvature may be caused by aggregation of MAXCalix in the organic phase. These aggregation processes are well known and described in the literature for other extractants.[26–29]

By using slope analysis, Figure 3 also provides information about the species which is formed during the extraction process. Based on the ligand

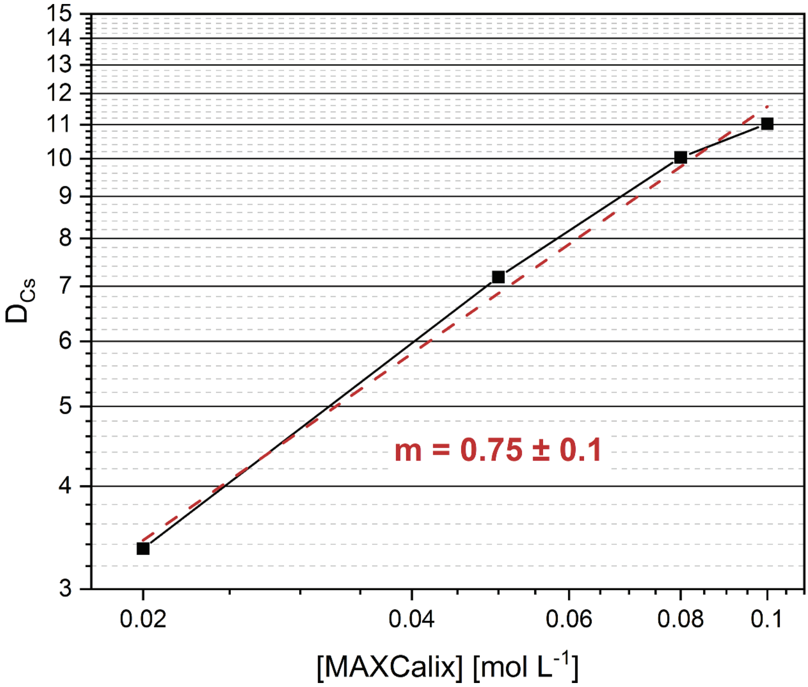

Figure 3. Cs^+ distribution ratios as a function of the extracting agent concentration. Org. phase: MAXCalix in 1-octanol/kerosene $75/25\%_v$. Aq. phase: [Cs-133] = 10^{-4} mol L^{-1}, [Cs-137] = 4 kBq - mL^{-1}, [NaCl] = 4 mol L^{-1}, [HNO_3] = 10^{-5} mol L^{-1}, pH_m = 3. A/O 1:1.

structure and prior results,[23] the formation of a 1:1 complex species is expected. The slope of 0.75 deviates from the expected value of 1, due to aggregation of MAXCalix, but nevertheless, indicates the formation of a 1:1 complex. A strong increase of organic phase viscosity with increasing MAXCalix concentration was observed. Since this impacts mass transfer and phase separation, a concentration of 0.05 mol L^{-1} MAXCalix was selected as a compromise between sufficiently high D_{Cs} values and adequate hydrodynamic properties.

Chloride concentration

The Cs^+ distribution was determined as a function of the chloride concentration (see Figure 4). In this case, NaCl was used as a chloride source to allow the comparison with the literature.[23] The extraction follows an almost linear trend with increasing NaCl concentrations with D_{Cs} values of $4{\cdot}10^{-2}$ at 0.001 mol L^{-1} NaCl and 7.2 at 4 mol L^{-1} NaCl. In conclusion, the extraction is driven by the chloride concentration in the aqueous phase. Cs^+ is extracted at NaCl concentrations above 0.2 mol L^{-1} NaCl. Compared to the available literature data this corresponds to an improvement in extraction performance.[23] The slope analysis provides a slope of 0.64

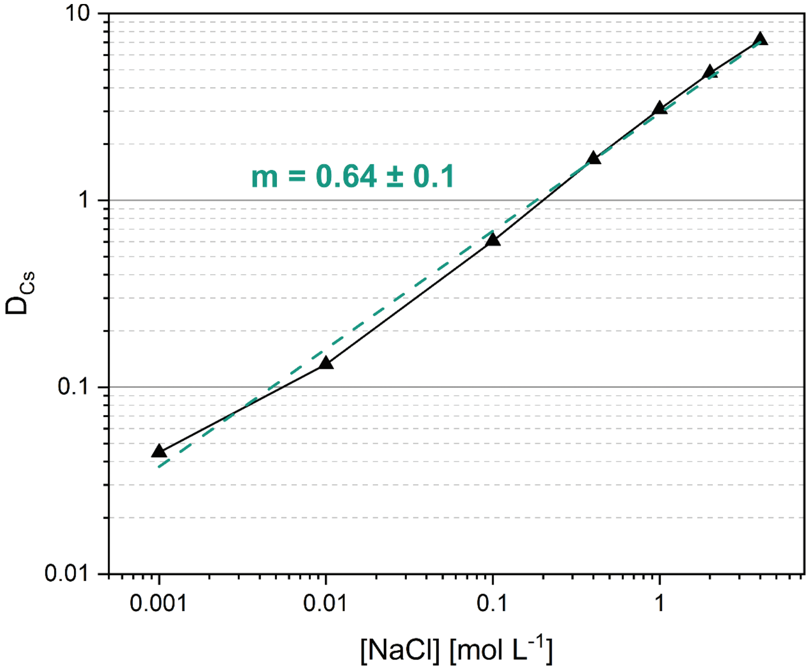

Figure 4. Cs^+ distribution as a function of the NaCl concentration. Org. phase: 1-octanol/kerosene 75/25%$_v$, [MAXCalix] = 0.05 mol L^{-1}. Aq. phase: [Cs-133] = 10^{-4} mol L^{-1}, [Cs-137] = 4 kBq mL^{-1}, [NaCl] = 10^{-3} – 4 mol L^{-1}, [HNO_3] = 10^{-5} mol L^{-1}, pH_m = 3. A/O 1:1.

which deviates from the expected value of one by a large margin. This may originate from differences in the activity coefficients and the presence of a small but constant concentration of NO_3^- (from the Cs-137 stock solution).

pH_m effect

To prevent adsorption or metal ion precipitation, the extraction should be performed from slightly acidic aqueous solutions. Accordingly, the pH dependency has been determined. Figure 5 shows D_{Cs} as a function of the pH_m value in the aqueous phase with [NaCl] = 0.4 and 4 mol L^{-1}. In the pH range of 2–6, D_{Cs} does not vary significantly, concluding that the pH does not have an impact on the extraction. As a following, we conducted all our following experiments at $pH_m = 3$.

Back extraction

Based on the presented results, the extraction shows the following equilibrium

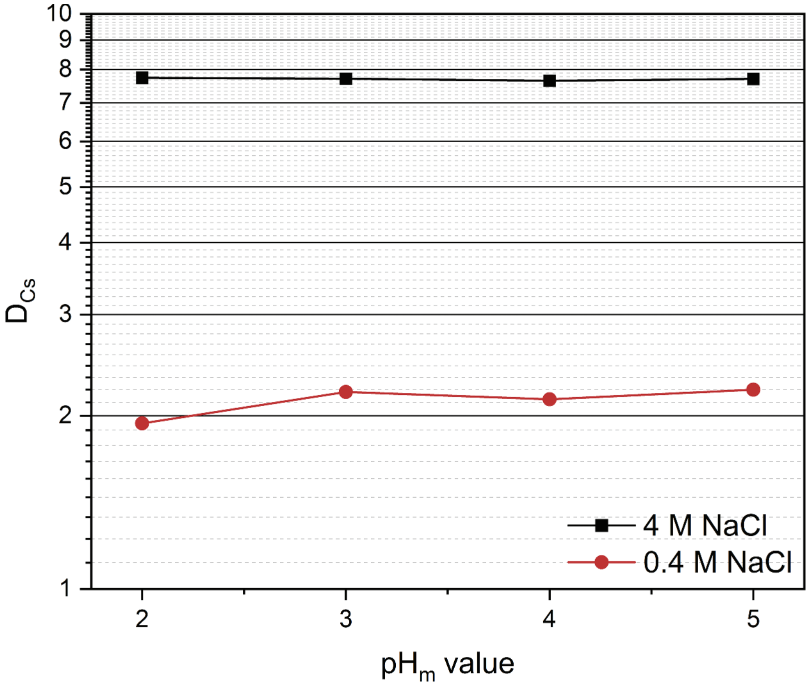

Figure 5. Cs^+ distribution ratios as a function of the pH_m for different NaCl concentrations. Org. phase: 1-octanol/kerosene 75/25%$_v$, [MAXCalix] = 0.05 mol L^{-1}. Aq- phase: [Cs-133] = $5 \cdot 10^{-4}$ mol L^{-1}, [Cs-137] = 4 kBq mL^{-1}, [NaCl] = 0.4, 4 mol L^{-1}. A/O 1:1.

$$Cs^{+}{}_{aq} + Cl^{-}{}_{aq} + MAXCalix_{org} \rightleftharpoons ([CsMAXCalix]Cl)_{org}$$

The Cs^+ extraction is driven by the chloride concentration. Thus, back extraction should take place at low chloride concentrations. To determine the optimal back extraction parameters, we extracted Cs^+ into the organic phase with $D_{Cs} = 5.2$ and then contacted the Cs^+ loaded phase with HCl solutions of varied concentration. The resulting Cs^+ distribution ratios are depicted in Figure 6 as a function of the HCl concentration. An effective back extraction (i.e. $D_{Cs} < 1$) is obtained with HCl concentration <0.3 mol L^{-1}. As already observed with NaCl, higher chloride concentrations in the aqueous phase lead to high D_{Cs} values up to 10, stabilizing the $[Cs(MAXCalix]^+$ complex in the organic phase.

Cs extraction in presence of MCl (M = Na^+, K^+, Mg^{2+}, Ca^{2+})

With the extraction parameters set, we focus on the extraction of Cs^+ in presence of Na^+, K^+, Ca^{2+} and Mg^{2+} which may be present in high concentrations in selected cases. Figure 7 depicts D_{Cs} as a function of the chloride concentration ($[MCl/MCl_2] = 10^{-3} - 4$ mol L^{-1}) using 0.05 mol L^{-1} MAXCalix in 1-octanol/kerosene 75/25%$_v$. For Na^+, Mg^{2+} and Ca^{2+} the D_{Cs} values are almost identical.

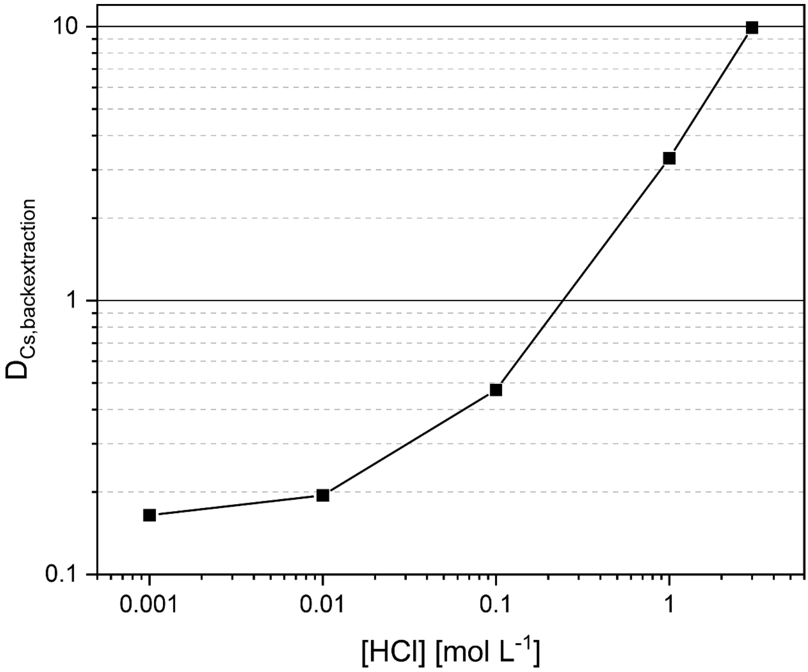

Figure 6. Cs^+ distribution ratios as a function of the HCl concentration in the aqueous phase. Back extraction was executed with an organic phase previously loaded with Cs^+. Org. phase: 1-octanol/kerosene 75/25%$_v$, [MAXCalix] = 0.05 mol L^{-1}. Aq. phase: [HCl] = $10^{-3} - 3$ mol L^{-1}. A/O 1:1.

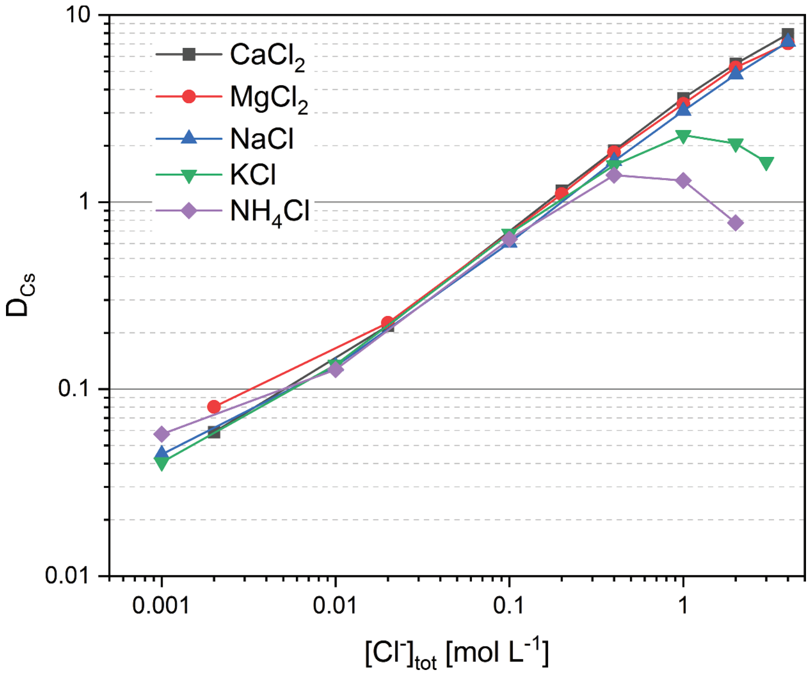

Figure 7. Cs^+ distribution ratios as a function of the chloride concentration in presence of Na^+, K^+, Mg^{2+}, Ca^{2+} and NH_4^+. Org. phase: 1-octanol/kerosene 75/25%$_v$, [MAXCalix] = 0.05 mol L^{-1}. Aq. phase: [Cs-133] = 10^{-4} mol L^{-1}, [Cs-137] = 4 kBq mL^{-1}, [MCl/MCl$_2$] = 10^{-3} – 4 mol L^{-1}, [HNO_3] = 10^{-5} mol L^{-1}, pH_m = 3. A/O 1:1.

At the highest chloride concentration, $[Cl^-] = 4$ mol L^{-1}, we obtained $D_{Cs}(Na) = 7.18$, $D_{Cs}(Mg) = 7.05$ and $D_{Cs}(Ca) = 7.9$, respectively. The linear increase of log D_{Cs} with log $[Cl^-]$ implies that neither Na^+ nor Mg^{2+} nor Ca^{2+} are co-extracted and thus do not influence the Cs^+ extraction.

In contrast to these ions, the presence of K^+ influences the Cs^+ extraction quite significantly. Up to $[Cl^-] = 0.4$ mol L^{-1}, the $D_{Cs}(K)$ values are comparable to $D_{Cs}(Na)$, $D_{Cs}(Mg)$ and $D_{Cs}(Ca)$. The highest D_{Cs} value is obtained at $[Cl^-] = 1$ mol L^{-1} with $D_{Cs} = 2.3$ which is approximately 60% lower compared to the other metal ion systems. Further increasing K^+ concentration leads to a decrease in the distribution ratio of Cs^+ to $D_{Cs} = 1.3$ at $[Cl^-] = 3$ mol L^{-1}. Clearly, K^+ influences strongly the extraction of Cs^+ at high chloride and potassium concentration. This is not surprising, since 18-crown-6 ethers form very stable complexes with K^+ cations.[30]

In addition to Na^+, K^+, Mg^{2+} and Ca^{2+}, the influence of NH_4^+ has been studied. NH_4^+ shows comparable properties as a pseudo alkali ion ($r(NH_4^+) = 148$ pm,[31] $r(K^+) = 138$ pm[32]) and therefore is interesting from a fundamental scientific point of view. Between $[NH_4Cl] = 0.001$ mol L^{-1} and $[NH_4Cl] = 0.4$ mol L^{-1} D_{Cs} increases almost linearly with increasing NH_4Cl concentration. No significant deviation of the distribution ratio is observed in comparison to the NaCl and KCl systems.

The highest D_{Cs} value of 1.4 is obtained at $[Cl^-] = 0.4$ mol L^{-1}. As observed for the KCl system, $D_{Cs}(NH_4)$ decreases significantly at higher NH_4Cl concentrations. Further analysis of the D_{Cs} values in the concentration range 0.4–3 mol L^{-1} show that even smaller D_{Cs} are obtained as for the K^+ system. This indicates a slightly better co-extraction of NH_4^+ compared to K^+ which arguably stems from the difference in ionic radius.

The previous study shows that K^+ might cause problems in Cs^+ extraction in environmentally relevant systems. To study K^+ co-extraction without the chloride effect, we conducted Cs^+ extraction experiments with varying K^+ concentrations using NaCl/KCl mixtures, whereas the chloride concentration remained constant at 3 mol L^{-1}. As presented in Figure 8, D_{Cs} decreases significantly from $D_{Cs} = 6.2$ in 3 mol L^{-1} NaCl to $D_{Cs} = 1.6$ in 3 mol L^{-1} KCl, confirming the competitive extraction of K^+.

Cs extraction from multicomponent brine solutions

After studying the individual influence of the components of brine solutions from a typical salt mine, extraction experiments of Cs^+ in the presence of an

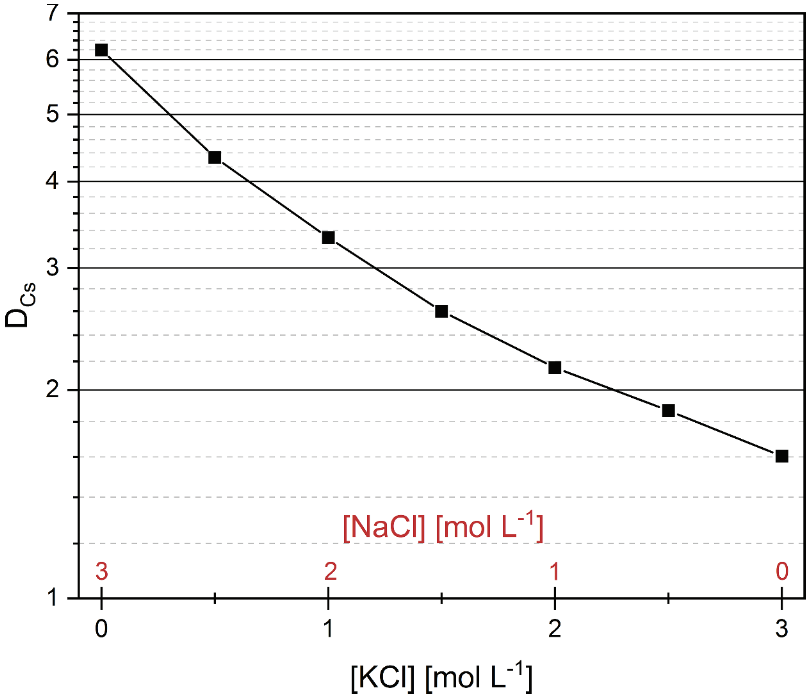

Figure 8. Cs^+ distribution ratios as a function of $[K^+]$ or $[Na^+]$ concentration in a NaCl/KCl mixture system with $[Cl^-]_{tot} = 3$ mol L^{-1}. Org. phase: 1-octanol/kerosene 75/25%v, [MAXCalix] = 0.05 mol L^{-1}. Aq. Phase: [Cs-133] = 10^{-4} mol L^{-1}, [Cs-137] = 4 kBq mL^{-1}, [KCl] = 0–3 mol L^{-1}, [NaCl] = 0–3 mol L^{-1}, $[Cl^-]_{tot} = 3$ mol L^{-1}, $[HNO_3] = 10^{-5}$ mol L^{-1}, $pH_m = 3$. A/O 1:1.

Table 1. Composition of the mixed brine solutions which are used to test Cs^+ separation in presence of Na^+, K^+, Mg^{2+} and Ca^{2+}. Salt concentrations are given in mol L^{-1}·.

Salts/Solution	S1	S2	S3	S4
$MgCl_2$	4.0	–	–	–
$CaCl_2$	–	3.9	3.8	2.5
KCl	0.5	0.7	0.8	0.9
NaCl	0.4	0.4	0.5	3.0
Cl^- (total)	8.9	8.9	8.9	8.9

electrolyte mixture have been performed. These solutions may be dominated by Mg^{2+}, Ca^{2+} or Na^{+}.[33] The K^+ concentration varies between 0.5 and 0.9 mol L^{-1} and the total chloride concentration is in all cases fixed at 8.9 mol L^{-1}. A detailed list of the salt composition of all mixed brine solutions used in these experiments is given in Table 1.

Initial extraction studies using S1-S4 have shown problems concerning the separation of the organic and aqueous phases after centrifugation due to the high salt load. To facilitate the phase separation, we diluted the initial aqueous phases by a factor of two resulting in in a total chloride concentration of 4.45 mol L^{-1}. Using the diluted aqueous phases, distribution ratios for all ions have been determined. The results are summarized in Table 2.

Table 2 shows that Cs^+ is selectively extracted from all mixed brine solutions. D_{Cs} values vary between 4 and 6 and are in general slightly lower than the values obtained from the individual component studies at chloride concentration of 4 mol L^{-1} (e.g D_{Cs}(4 mol L^{-1} NaCl) = 7.2). This difference clearly originates from the presence of K(I) in the aqueous phase. Furthermore, D_{Cs} decreases with increasing K^+ concentration which is in line with our results as previously discussed. However, D_K values are in the range of $3.8{\cdot}10^{-2}$ – $4.8{\cdot}10^{-2}$ which provides a separation factor of Cs^+ over K^+ of $SF_{Cs/K} > 100$. In conclusion, Cs^+ is effectively separated from K(I) under these conditions. Cs^+ is even better separated from Na^+ with D_{Na} values of $1.6–6{\cdot}10^{-3}$ ($SF_{Cs/Na} \approx 10^3$) and from Mg^{2+}/Ca^{2+} ($D_{Mg}/D_{Ca} = 2–4{\cdot}10^{-4}$; $SF_{Cs/Mg}/SF_{Cs/Ca} \approx 10^4$). This is in line with the previously discussed results where neither Na^+ nor Mg^{2+} nor Ca^{2+} competes with Cs^+ extraction.

Table 2. Distribution ratios for various metal ions from extraction experiments using 1:1 diluted mixed brine solutions S1-S4. Org. Phase: 1-octanol/kerosene 75/25%v, [MAXCalix] = 0.05 mol L-1. Aq. Phase: [Cs-133] = 10^{-4} mol L^{-1}, [Cs-137] = 4 kBq mL^{-1}, [MCl/MCl_2] see Table 1 (1:1 diluted), $[Cl^-]_{tot} = 4.45$ mol L^{-1}, [HNO_3] = 10^{-5} mol L^{-1}, $pH_m = 3$. A/O = 1:1. Analysis methods: Cs-137/Na-22 = γ-counter; Cs-133: FAES; Na, K, Mg, Ca = ICP-OES.

D(M)/solutions	S1	S2	S3	S4	$SF_{Cs/M}$
Cs	5.71	5.00	4.72	4.79	
Mg	0.0004	–	–	–	$>10^4$
Ca	–	0.0002	0.0002	<LOD	$>10^4$
K	0.038	0.034	0.031	0.048	>100
Na	0.0033	0.0017	0.0016	0.006	$>10^3$

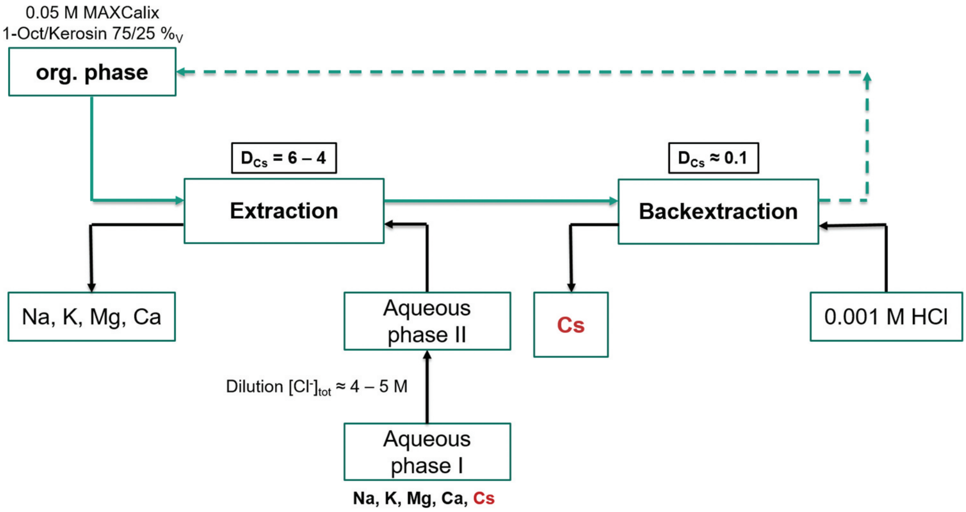

Figure 9. Simplified flow sheet based on the results presented in this study.

The distribution ratios of Na^+, K^+, Mg^{2+} and Ca^{2+} provide valuable information on the coordination chemistry of MAXCalix. The experimental data show that there is a correlation between ionic size and distribution ratio. The largest cation, Cs^+, forms indisputably the strongest complex, followed by K^+ and Na^+. The minute extraction of Mg^{2+} and Ca^{2+} may be due to the diluent itself, as obvious when comparing the distribution ratios from the extraction by the extracting agent (Table 2) and extraction by the diluent (c.f supporting information Table S1). In consequence, neither Mg^{2+} nor Ca^{2+} are expected to form complexes with MAXCalix.

Taking all the data into account, an extraction scheme has been developed (see Figure 9). In the first step, the saline solution is diluted to a chloride concentration of 4–5 mol L^{-1}. The diluted aqueous phase is then contacted with the organic phase (ratio 1:1) containing 0.05 mol L^{-1} MAXCalix dissolved in 1-octanol/kerosene 75/25%$_V$. Cs^+ is extracted into the organic phase with D_{Cs} values of 4–6. Na^+, K^+, Ca^{2+} and Mg^{2+} remain in the aqueous phase. Back extraction of Cs(I) is achieved using 0.001 mol L^{-1} HCl with $D_{Cs} \approx 0.1$.

Conclusions

In this study, we propose a procedure for efficiently separating radioactive Cs^+ from brine solutions on the laboratory scale by using liquid-liquid extraction. Cs^+ extraction using MAXCalix is accomplished with chloride concentrations exceeding 0.3 mol L^{-1}. The efficiency of extraction notably improves at higher chloride concentrations, resulting in Cs^+ distribution ratios ranging between 4 and 6 at $[Cl^-] = 4.45$ mol L^{-1}, depending on the composition of the aqueous phase. Separation factors determined from these mixed brine solutions containing Na^+, K^+, Ca^{2+}, and Mg^{2+} range between 10^4 and 100.

The established procedure is sensitive to the presence of K^+, however, also features substantial tolerance margins against other alkali or earth alkali cations. This is important since the composition of the feed solution may vary strongly for different systems. Nonetheless, the presented results show that Cs^+ extraction is still feasible even at high K^+ concentrations, emphasizing the strengths of the developed procedure.

Disclosure statement

No potential conflict of interest was reported by the author(s).

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