Selective Removal of $^{226}Ra^{2+}$ from Gas-Field-Produced Waters

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The $^{226}Ra^{2+}$ selectivity of both the self-assembled (iso)-guanosine-based systems and ionizable thiacalix[4]crown dicarboxylic acids was determined in gas-field-produced water and a metal ion-containing model solution (simulant). Seven gas-field-produced water samples have been analyzed. From a sample (K5D) with average metal ion concentrations ([metal$_{tot}$] = 0.14 M), thiacalix[4]crown-5 dicarboxylic acid (10^{-4} M) extracts 60% of the $^{226}Ra^{2+}$ content. Extractions performed with the model solution (^MK5D) indicate that in K5D there is significant competition in $^{226}Ra^{2+}$ extraction due to the organic constituents of K5D, in particular with self-assembled extractants guanosine and isoguanosine. Nevertheless, all four extractants extract $^{226}Ra^{2+}$ both from the produced water K5D and the model solution ^MK5D, even with a 100-fold excess of [metal$_{tot}$] to [extractant]. The extracted $^{226}Ra^{2+}$ cations could effectively be stripped from the extractants by washing with pH 2 water. The results obtained with the extractants used, especially thiacalix[4]crown-5 dicarboxylic acid **3**, clearly demonstrate the way to selectively remove Ra^{2+} from gas-field-produced waters.

Introduction

Sedimentary rocks containing oil and gas deposits may contain the naturally occurring (*1*) nuclides ^{238}U and ^{232}Th (*2*) and Ra^{2+} holding formation water (*3*, *4*). This Ra^{2+} containing formation water is transported to the surface together with, for example, sulfate-rich injected (sea) water (*5*, *6*). At the surface, a part of the Ra^{2+} precipitates in sulfate-rich scales and sludges, while the rest is introduced into the

environment with the produced water (*7*). According to the OSPAR convention's recommendations (2001), the oil and gas industries have to reduce the emission of naturally occurring materials to near background levels by 2020 (*8*), while the Ra^{2+} concentration of produced water is currently about 3 times higher than in normal seawater (*9*). Furthermore, Ra^{2+} and its daughter nuclides Rn, Po, and Pb can be ingested, for example, via seafood consumption (*7*), and consequently can induce cancer (*10*). In The Netherlands, a release of 10 GBq/yr of $^{226}Ra^{2+}$ into the environment is allowed (*11*) since only a low dose is obtained from this nuclide (*7*). However, the most important contribution to the annual dose of the world's population is caused by the direct daughter nuclide of $^{226}Ra^{2+}$, namely, the radioactive ^{222}Rn gas (*12*), which is assumed to cause around 20 000 lung cancer deaths per year in the United States (*13*). Therefore, we feel that selective extraction of Ra^{2+} from produced water effluents such as those of the (oil and) gas industry is of utmost importance.

The highly toxic nature of Ra^{2+} isotopes renders effective separation of these radionuclides from other nontoxic substances highly desirable. A commonly used technique to analyze the Ra^{2+} content of water streams is the nonspecific binding of alkaline earth cations on manganese/titanium oxide (*14*, *15*). Furthermore, the properties of Ra^{2+} cations can also be used to immobilize them in synthetic clay such as Na-4-mican (*16*). However, none of these techniques have shown to be Ra^{2+} selective in the presence of an excess of chemically identical alkaline earth cations as compared to the amount of extractant used. In previous studies we have shown that both the non-covalent self-assembly of guanosine (**1**) and isoguanosine (**2**) subunits (*17*) and the covalent self-neutralizing thiacalix[4]crown-5 dicarboxylic acid **3** and thiacalix[4]crown-6 dicarboxylic acid **4** (*18*) provide excellent $^{226}Ra^{2+}$ selective extractants in the presence of up to a 35×10^6 fold excess of the most abundant alkali(ne earth) cations (*19*).

A significant challenge is the selective extraction of Ra^{2+} (average concentration 5.9−9.0 Bq/L) (*7*) from, for example, gas-field-produced waters containing a large excess of other, mainly alkali(ne earth), cations (*19*) and anions (e.g., SO_4^{2-}, Cl^-, and HCO_3^-) (*20*). Literature studies suggest that these waters also contain a wide variety of organic species, such as oil, monocyclic aromatic hydrocarbons, and fatty acids (*19−21*). In addition, commonly used water-soluble scale inhibitors such as different types of phosph(on)ates, carboxylates, and sulfonates can be present (*20*). In this paper we focus on the influence of metal ions on the $^{226}Ra^{2+}$ extraction.

In this paper we show the potential use of extractants (**1−4**; Figure 1) with a high $^{226}Ra^{2+}$ selectivity, under laboratory conditions, for the extraction of Ra^{2+} from industrial-produced water. To the best of our knowledge, this is the first time that this problem has been addressed with selective extractants.

Experimental Section

Materials. The preparation of guanosine (**1**) (*22*), isoguanosine (**2**) (*23*), thiacalix[4]crown-5 dicarboxylic acid (**3**) (*17*) and thiacalix[4]crown-6 dicarboxylic acid (**4**) (*17*) was according to literature procedures. Tris(hydroxymethyl)aminoethane (tris) 99.8+% was ordered from Aldrich. The acids (concentrated HCl and HNO_3) and CH_2Cl_2 were of pro analysis (p.a.) grade and used as received. The nitrate salts of K$^+$ (≥99.5%), Rb$^+$ (p.a.), and Mn^{2+} (≥97.0%) were purchased from Fluka Chemie and Na$^+$ (p.a.), Cs$^+$ (99%), Mg^{2+}(p.a.),

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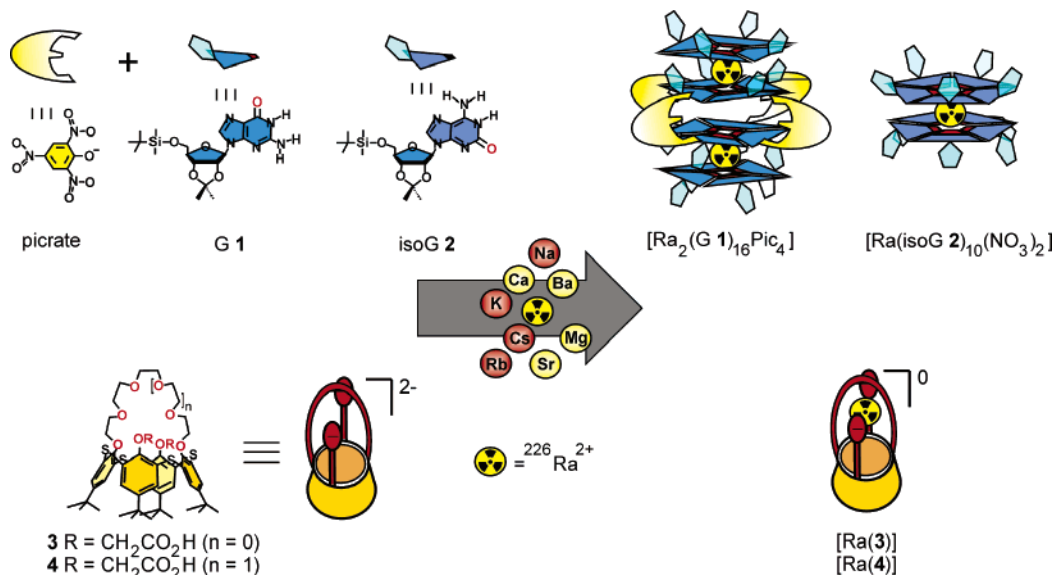† University of Twente.
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FIGURE 1. Selective Ra^{2+} extractants and their expected Ra^{2+} complexation. Both G 1 and isoG 2 form selective Ra^{2+} extractants by way of (in situ) self-assembly, while the thiacalix[4]crown dicarboxylic acids 3 and 4 provide "custom-made" extractants with an optimized Ra^{2+} coordination cage.

Ca^{2+} (p.a.), Sr^{2+} (p.a.), Ba^{2+} (p.a.), Cd^{2+} (98%), Zn^{2+} (98+%), Pb^{2+} (p.a.), and Fe^{3+} (>99%) were purchased from Acrôs Organics. $^{226}Ra^{2+}$ stock solutions were purchased from AEA Technology QSA GmbH; ^{226}Ra was used due to its long half-life ($t_{1/2} = 1.6 \times 10^{3}$ yr). **(Note: ^{226}Ra has a very high radiotoxicity and should be handled with care and under radionuclear supervision).**

Solutions. All basic experiments were performed using an organic phase containing 10^{-4} M extractant in CH_2Cl_2. The extractant concentrations of the organic solutions were based on the amount of "free" extractant needed to complex one alkaline earth cation [$(1)_8$, $(2)_{10}$, 3, and 4]. Produced water samples were used as obtained from the gas well. To directly compare the extraction data with previous results (17, 18), the K5D metal ion-based model solution was made using metal nitrate salts, Na^+ (5.7×10^{-1} M), K^+ (2.3×10^{-3} M), Mg^{2+} (1.5×10^{-2} M), Ca^{2+} (1.1×10^{-1} M), Sr^{2+} (1.5×10^{-3} M), Ba^{2+} (1.8×10^{-5} M), Fe^{3+} (1.5×10^{-3} M), Mn^{2+} (1.2×10^{-4} M), and Zn^{2+} (3.9×10^{-5} M), in demineralized water. Produced water (model solution) dilutes (5, 20, 50, 70, and 100 times) were made in a pH 8.9 Tris-HCl buffer since previous work has shown that the extractants used only show quantitative $^{226}Ra^{2+}$ extraction above pH 8 (17, 18). From stock solution of $^{226}Ra^{2+}$ in 0.5 M HCl, containing no carrier (e.g., Ba^{2+}), a dilution of 12 kBq/g (1.4×10^{-6} M) in 0.1 M HNO_3 was made.

Determination of the Metal Ion Contents of Produced Water Samples (Table 1). The produced water samples were diluted 10 times in Milli-Q water, after which 0.5 mL of concentrated nitric acid and 0.1 mL of internal standard were added. The determination of the Mg, Ca, Ba, Sr, Fe, Mn, Zn, Pb, U, Tl, Te, Cd, Ag, Mo, Cu, Ni, Co, Ti, and Be metal ion content was performed using a Perkin-Elmer Sciex Instruments Elan 6000 inductively coupled plasma mass spectrometer (ICP-MS) equipped with a cross-flow nebulizer, a platinum sampler, and a skimmer cone. Analysis was performed with the following: Ge and Re as internal standards, a power of 900 W, a nebulizer gas flow of 0.87 L/min, a plasma gas flow of 15 L/min, and a sample uptake of 1 mL/min. Interference corrections were made for $^{40}Ca^{16}OH^+$ on $^{57}Fe^+$, $^{43}Ca^{16}O^+$ on $^{59}Co^+$, $^{43}Ca^{16}O^+$ on $^{60}Ni^+$, sulfur on $^{65}Cu^+$, and $^{66}Zn^+$ and $^{88}Sr^{2+}$ on $^{44}Ca^+$. Seven callibration standards were used, ranging from 0.1 to 50 μg/L (in the case of Mg, Fe, and Zn the concentrations used were

TABLE 1. Metal Ion Content of Seven Produced Water Samples[a]

metal ion	range [M]	average [M]	K5D [M]
Ti^b	9.4×10^{-10}–1.1×10^{-6}	2.3×10^{-7}	3.3×10^{-7}
Mn^b	2.3×10^{-6}–5.0×10^{-4}	9.6×10^{-5}	1.2×10^{-4}
Fe^b	2.6×10^{-4}–5.4×10^{-3}	1.4×10^{-3}	1.5×10^{-3}
Co^b	1.4×10^{-7}–5.6×10^{-7}	3.1×10^{-7}	2.3×10^{-7}
Ni^{2+}	($<1.7 \times 10^{-8}$)–1.7×10^{-6}	9.0×10^{-7}	1.1×10^{-7}
Cu^b	8.8×10^{-9}–1.4×10^{-6}	3.8×10^{-7}	3.2×10^{-7}
Zn^{2+}	($<3.1 \times 10^{-7}$)–2.3×10^{-3}	3.9×10^{-4}	3.9×10^{-4}
Cd^{2+}	4.5×10^{-11}–3.3×10^{-6}	5.5×10^{-7}	4.9×10^{-7}
Tl^{3+}	3.6×10^{-10}–7.4×10^{-7}	1.3×10^{-7}	1.7×10^{-7}
Pb^b	($<4.0 \times 10^{-8}$)–1.6×10^{-4}	2.4×10^{-5}	1.3×10^{-5}
total transition metal cations		1.9×10^{-3}	2.0×10^{-3}
Mg^{2+}	($<2.1 \times 10^{-6}$)–5.0×10^{-2}	9.9×10^{-3}	1.5×10^{-2}
Ca^{2+}	2.1×10^{-6}–3.8×10^{-1}	7.2×10^{-2}	1.1×10^{-1}
Sr^{2+}	6.3×10^{-8}–6.2×10^{-3}	1.1×10^{-3}	1.5×10^{-3}
Ba^{2+}	3.5×10^{-8}–1.4×10^{-4}	2.5×10^{-5}	1.8×10^{-5}
Na^+	3.1×10^{-4}–2.1	4.1×10^{-1}	5.7×10^{-1}
K^+	6.1×10^{-6}–4.1×10^{-3}	1.4×10^{-3}	2.3×10^{-3}
total alkali(ne earth) cations		4.9×10^{-1}	7.0×10^{-1}
total		5.0×10^{-1}	7.0×10^{-1}

[a] Range of concentrations, average concentration, and sample K5D determined with ICP-MS and in the case of Na^+ and K^+ with a flame photometer. Metal ions with an average concentration below 10^{-7} M are not reported. [b] These metal ions can be present in a number of valencies.

a factor 10 higher). The distribution of the found values is 10% with the exception of Cu, Zn, Co, and Ni, which give 15%, and Be, Ag, Fe, Te, and Mg, which give 20%.

The analysis of the Na and K metal ion content was performed using an Eppendorf ELEX 6361 flame photometer. Eight calibration standards were used, ranging from 50 to 2500 mg/L for Na and from 10 to 250 mg/L for K. The distribution of the found values is 5% for Na and 10% for K.

$^{226}Ra^{2+}$ Extraction Procedures (Figure 2). Equal volumes (2.0 mL) of the organic and aqueous solutions were transferred into a screw cap vial with a volume of 4 mL. To determine the $^{226}Ra^{2+}$ extraction, 40 μL of $^{226}Ra^{2+}$ tracer (480 Bq) was added to the aqueous phase (2.8×10^{-8} M). Because experiments performed with half the amount of tracer still give the same extraction percentages, the $[metal_{tot}]/[extractant]$ ratio probably has a larger influence on the $^{226}Ra^{2+}$ extraction than the concentration of $^{226}Ra^{2+}$ tracer in
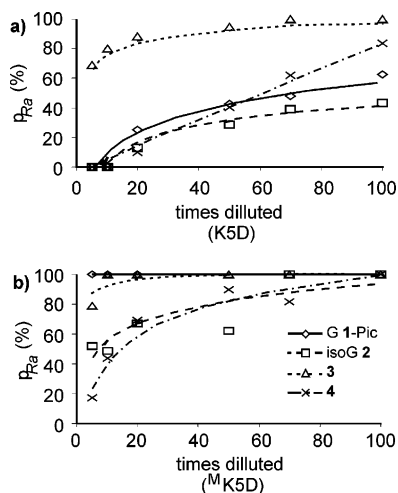
FIGURE 2. $^{226}Ra^{2+}$ extraction percentages ($p_{Ra} = 100\% \times [^{226}Ra^{2+}]_{org}/[^{226}Ra^{2+}]_{tot}$) vs times of dilution: (a) produced water sample K5D and (b) metal ion-based model solution $^{M}K5D$ (expected errors between 10 and 15%). Markers depict experimentally obtained points, while the trend lines merely provide a guideline for the eye.
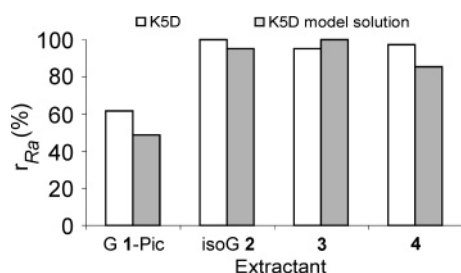

FIGURE 3. Average $^{226}Ra^{2+}$ recovery (r_{Ra}) from the extractants 1−4. Stripping of a 1 mL organic phase occurred with a 1 mL pH 2 aqueous phase (HCl).

the aqueous phase. In the case of the guanosine (**1**) extraction experiments two equivalents, compared to [(**1**)$_8$], of lithium picrate were added to allow for full extraction (*17*). The samples were shaken (1500 rpm) at ambient temperatures (22−24 °C) for 1 h to ensure complete settling of the two-phase equilibration. After extraction, the solutions were disengaged by centrifugation (1600 rpm for 5 min), and aliquots (0.5 mL) of the organic and aqueous phases were pipetted out for the determination of the $^{226}Ra^{2+}$ extraction percentages. The γ-activity (186 keV) was determined with a HPGe detector using a counting time of 2 h and a counting error of 10%. The obtained extraction percentages are defined as 100% times the ratio of activity in the organic phase (A_o) and the total activity ($A_o + A_{aq}$) (eq 1), with an estimated error between 10 and 15% (combination of the 10% error of the HPGe detector and a 10% human error) (*17, 18*):

$$p_{Ra}\% = 100\%(A_o/(A_o + A_{aq})) \qquad (1)$$

$^{226}Ra^{2+}$ Stripping Procedures (Figure 3). From the remaining 1.5 mL organic phase, a 1.0 mL sample was removed and transferred into a new screw-cap vial with a volume of 4 mL. Subsequently, 1.0 mL of pH 2 adjusted water (HCl) was added, and the samples were shaken (1500 rpm) at ambient temperatures (22−24 °C) for 1 h to ensure complete settling of the two-phase equilibration. After extraction, the solutions were disengaged by centrifugation (1600 rpm for 5 min), and an aliquot (0.5 mL) of the aqueous phases was pipetted out for the determination of the $^{226}Ra^{2+}$ stripping percentages. The obtained extraction percentages are defined as 100% times the ratio of activity in the aqueous stripping phase (A_{strip}) and the original activity in the organic

phase (A_{org}) (eq 2), with an estimated error of 10−15% (*17, 18*):

$$r_{Ra}\% = 100\%(A_{strip}/A_{org}) \qquad (2)$$

Produced Water Sampling. The produced water samples were taken downstream of the secundary water-treatment equipment and supplied in polythene sampling bottles of 1 L. The samples were not treated in anyway.

Results and Discussion

Metal Ion Constituents of Gas-Field-Produced Water. Since the content of produced waters can vary greatly around the world, we limited our study to gas wells at the Dutch continental shelf, which have been studied extensively for their organic substituents (*19*). Instead of measuring a lot of different samples, seven different gas-field-produced waters were analyzed using ICP-MS and a flame photometer.

Table 1 clearly shows the wide variety of cations present in the produced waters. Apart from traces of transition and other heavy metals (total 2×10^{-3} M) significant quantities of alkali(ne earth) cations are present (total 7×10^{-1} M). Of the latter the alkali cation Na^+ is by far the most abundant. Of the alkaline earth cations Ca^{2+} is the most abundant, followed by Mg^{2+}, Sr^{2+}, and Ba^{2+}. On the basis of the average metal ion concentrations, one produced water sample (K5D), which had metal ion concentrations closest to the average values was selected for further extraction experiments. For data of the separate samples see the Supporting Information.

$^{226}Ra^{2+}$ Extraction from a Produced Water Sample. Although liquid−liquid extraction would not provide a commercially effective procedure for actual $^{226}Ra^{2+}$ extraction, it is an effective method to assess the $^{226}Ra^{2+}/M_{tot}$ separation from gas-field-produced waters. From literature it is known that related extractants give highly identical selectivities in both liquid−liquid extraction systems and in commercially more effective separation systems such as supported membranes or functionalized solid supports (*24−26*). Although the Ra^{2+} extraction efficiency will improve with extractant concentrations that are equal to those of the total metal ion content, liquid−liquid extractions were performed with 10^{-4} M extractant [(**1**)$_8$, (**2**)$_{10}$, **3**, and **4**]. This extractant concentration allows for a direct comparison of the obtained extraction percentages with previous results, dealing with the $^{226}Ra^{2+}/metal_{single}$ selectivity in the alkali(ne earth) cation series (*17, 18*). However, as a consequence a number of dilution steps are required (5−100 times; samples K5D$_{1/5}$ − K5D$_{1/100}$), in a Tris buffer ([Cl^-] = 0.7×10^{-3} M), to determine the $^{226}Ra^{2+}$ extraction efficiency for [metal$_{tot}$]/[extractant] ratios ranging from 1400 to 70.

The extraction data (Figure 2a) show that with extractant **3**, about 70% of $^{226}Ra^{2+}$ can be extracted from K5D$_{1/5}$, whereas K5D$_{1/70}$ allows for quantitative extraction of $^{226}Ra^{2+}$. However, the other three extractants, **1**, **2**, and **4**, only extract $^{226}Ra^{2+}$ from the samples K5D$_{1/20}$ − K5D$_{1/100}$. In the case of K5D$_{1/100}$, these extractants only give $^{226}Ra^{2+}$ extraction percentages of 83%, 62%, and 43%, respectively. These results clearly show that the thiacalix[4]crown-5 dicarboxylic acid (**3**) is the best $^{226}Ra^{2+}$ extractant under these conditions, a result that is underlined by its effectivenes without any additives such as picrate anions.

To isolate the influence the metal ions in K5D have on the $^{226}Ra^{2+}$ extraction of the possible influence of anionic/organic substituents, extractions were performed with a metal ion-based model solution ($^{M}K5D$). This model solution contains the same concentration of the major metal ions present in produced water sample K5D, viz., Na^+, K^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Fe^{3+}, Mn^{2+}, Zn^{2+}, and Pb^{2+} (Table 1), resulting in a total metal ion concentration ([metal$_{tot}$]) of 0.70 M.

The highest $^{226}Ra^{2+}$ extraction percentages were obtained with the extractants **1** and **3**, showing (near) quantitative $^{226}Ra^{2+}$ extraction from $^MK5D_{1/5}$ (Figure 2b). This means that 10^{-4} M of extractant is able to extract 2.8×10^{-8} M $^{226}Ra^{2+}$ from a total salt concentration of 0.11 M. Surprisingly, the extractants previously reported to have the highest *overall* $^{226}Ra^{2+}$ selectivities in the alkali(ne earth) series, extractants **2** (*17*) and **4** (*18*), gave the poorest results with K5D and ^MK5D. Apparently, for these extractants there is more competition by the other cations present; competition by transition metal ions is not expected since the extractants only have hard donor atoms. Nevertheless, from $^MK5D_{1/70}$, all four extractants quantitatively extracted $^{226}Ra^{2+}$. This means that they can extract $^{226}Ra^{2+}$ at a [metal$_{tot}$]/[extractant] ratio of 100.

The extractants with the highest $^{226}Ra^{2+}/Na^+_{single}$ selectivity (**1** and **3**) show the highest $^{226}Ra^{2+}$ extraction from ^MK5D (Figure 2b) (*17, 18*). In $^MK5D_{1/5}$ the concentrations of the other alkali(ne earth) cations (Table 1), in particular that of the second most abundant cation Ca^{2+} (1.1×10^{-1} M), are below the previously determined thresholds for $^{226}Ra^{2+}$ extraction (*17, 18*). Of the extractants used, the lowest $^{226}Ra^{2+}/Ca^{2+}_{single}$ separation in the presence of only Ca^{2+} as single competing cation has been reported for extractant **2** (*17*); at 2.4×10^{-2} M Ca^{2+}_{single} still 30% of $^{226}Ra^{2+}$ is extracted (*17*). Apparently, Na^+ is the metal ion, which causes the competition in the $^{226}Ra^{2+}$ extraction.

The extraction data of K5D (Figure 2a) clearly show a lower $^{226}Ra^{2+}$ extraction efficiency than the ^MK5D model solution (Figure 2b). An increased competition in $^{226}Ra^{2+}$ extraction is observed for all four extractants; however, it is most pronounced with extractant **1**. It indicates that either anionic or organic constituents of K5D have a negative influence on the $^{226}Ra^{2+}$extraction. The anions are assumed to have no effect on the extraction behavior, since the extractants **1** (*17*), **3** (*18*), and **4** (*18*) provide their own anionic groups for neutralization; the extraction behavior of extractant **2** is even anion independent (*27, 28*). At K5D$_{1/100}$ and $^MK5D_{1/100}$ there still are distinct differences in the $^{226}Ra^{2+}$ extraction behavior. Due to dilution in a Tris-HCl buffer, [Cl^-] is equal to [metal$_{tot}$] in both samples (7×10^{-3} M). Therefore, the organic pollutants, such as fatty acids, reported in ref *8* to be present in produced waters on the Dutch continental shelf are thought to cause competition in the $^{226}Ra^{2+}$ extraction. A result that is in agreement with the formation of a "soapy" third phase, when the K5D sample is diluted less than 70 times, while the ^MK5D does not show such a behavior. It is important to note, that in a solid-support based extraction system, a soapy third phase will not be formed and will not influence the extraction equilibria. Consequently, the extractants **1**, **2**, and **4** might be much more effective in water streams, which do not contain competing organic constituents but have Na^+, Mg^{2+}, and Ca^{2+} as the main competing ions (*29, 30*).

Stripping of the Organic Phases. Efficient extraction of $^{226}Ra^{2+}$ depends on effective stripping from the organic phases into another aqueous solution (pH 2). Previously, it has been shown that the $^{226}Ra^{2+}$ extraction of all four extractants used cannot occur below pH 2 (*17, 18*). Therefore, $^{226}Ra^{2+}$-stripping experiments were performed at pH 2 with samples of the organic phases obtained after the $^{226}Ra^{2+}$ extraction experiments (see above; Figure 2). Average stripping percentages are shown in Figure 3.

The stripping experiments show that while extractant **1** only gives ~50% recovery, the other three extractants (**2**–**4**) exhibit near quantitative $^{226}Ra^{2+}$ recoveries under the conditions used. This means that these extractants are not only able to selectively extract $^{226}Ra^{2+}$ cations but can also effectively be stripped of their radioactive radium content. The complete regeneration of the extractants **4** (and **3**) has

been reported (*18*), indicating that after stripping these extractants can effectively be reused for the extraction of $^{226}Ra^{2+}$ from aqueous solutions with a pH above 8.

Supporting Information Available

The analysis results of the seven different gas-field-produced samples. This material is available free of charge via the Internet at http://pubs.acs.org.

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