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Selective Rejection of Dissolved Uranium Carbonate from Seawater Using Cross-Flow Filtration Technology

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Abstract: Cross-flow membrane filtration equipment was operated to evaluate the selective uranium carbonate rejection from seawater of different flat sheet membranes. The membranes were discriminating by the rejection of uranium, calcium, and sodium under geochemical conditions that mimic uranium in seawater. Then, operating parameters were optimized, and the selective rejection of dissolved uranium was checked on prefiltrated seawater. Concentration factors of 1.1 and 8.5 for sodium and uranium(VI), respectively, were obtained for a nanofiltration volume ratio of 0.96.

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INTRODUCTION

There is an extensive literature on equilibria involved in the uranium-carbonate systems (1, 2). Uranium(VI) carbonate systems are usually quite complicated in that they consist of several different complex ions in rapid equilibria with one another and with the aquo-ion or hydrolyzed species. At a low uranyl concentration and when this concentration does not exceed the carbonate concentration, monomeric uranyl carbonate species $UO_2(CO_3)$, $UO_2(CO_3)_2^{2-}$ and $UO_2(CO_3)_3^{4-}$ are expected to dominate above pH 5. A speciation diagram was built with the aid of the CHESS software (3). In a solution containing 1×10^{-5} M UO_2^{2+} and 2×10^{-3} M (CO_3^{2-}, HCO_3^-) the neutral complex $UO_2(CO_3)$ dominates the system at pH 5.5, but at a sea water pH of 8.3, $UO_2(CO_3)_2^{2-}$, and $UO_2(CO_3)_3^{4-}$ are the major species (Fig. 1). However, there is no experimental evidence for the presence of this bulky ion in natural seawater due to its extremely low concentration of about 3 μg/L (4–6).

The general feature with nanofiltration membranes is separation of salts according to their size and valency. Thus, a high-retention coefficient of this bulky (7) and highly charged U(VI) species can be expected (8).

The purpose of the present study is to assess the possibilities of cross-flow technology in selectively concentrating uranium from seawater. In the first step, the ability of various nanofiltration (NF) or low-ultrafiltration (L-UF) membranes to selectively reject uranium is evaluated. Next, the operating parameters, transmembrane pressure, and tangential velocity are optimized to increase uranium rejection. Then, the nanofiltration apparatus is used for the diafiltration of uranium from prefiltrated seawater.

EXPERIMENTAL SECTION

Reagents and Experimental Conditions

Deionized water was used for the preparation of all the stock solutions and for membrane performance experiments. Solutions were prepared using uranium salts, $UO_2(NO_3)_3 \cdot 6H_2O$ (Prolabo), sodium chloride, sodium carbonate, sodium hydroxide, and calcium chloride (Acros). Synthetic seawater was prepared by introducing 1×10^{-5} M uranyl nitrate, $UO_2(NO_3)_2$, to distilled water containing 2×10^{-3} M Na_2CO_3. The pH of the solution was then adjusted to 8.3 with diluted sodium hydroxide and addition of 0.18 M of NaCl and 9×10^{-3} M $CaCl_2$. Prefiltered (5 μm) seawater was supplied by the Institut National des Sciences et Techniques de la Mer, Digue de Collignon, BP 324, 50130 Cherbourg-Octeville Cedex, France.

Membrane

The commercial membranes Desal 5DL, G-10, and G-20 (Osmonics) tested are flat membranes made of polyamide filtering layers. The membrane area is 150 cm^2, and the characteristics of the membranes are listed in Table 1. Before starting experiments, the membrane is activated and conditioned as described (9).

Nanofiltration Apparatus

Nanofiltration experiments were performed with Osmonics Sepa CF lab-scale membrane cell and a schematic flow diagram of the lab-scale membrane system as presented in Fig. 2. The membrane cell is composed of two elements (cell body and cell holder). The feed stream is pumped from the feed tank to the cell body. The solution flows tangentially across the membrane surface. A heat exchanger controls the experiments temperature. Hydraulic parameters were monitored using pressure gauges and flow meters. The pH was measured with a combined pH electrode by using a KS120 (Radiometer Analytical) glass electrode saturated with a KCl + AgCl solution.

For the characterization of the retention coefficient of the membrane, the feed is maintained at constant composition during the experiments by totally recycling the permeate and the retentate (valve 12 open). For dialfiltration experiments, the valve 13 is opened, and the retentate is recovered in tank 11.

Rejection Analysis

Rejections of ions were determined from the measured feed and permeate concentrations of samples collected during the course of the experimental tests. The retention (R%) was calculated as follows: $R = 100 \times (1 - C_p/C_f)$, where C_f is the concentration in the feed and C_p is the concentration in the permeate.

Uranium, sodium, and calcium determination was performed by Inductively Coupled Plasma Atomic Emission Spectrometry (Spectro D, ICP

Table 1. Characteristics of the membranes studied

	5DL	G-10	G-20
Molecular weight cut-off (MWCO)	150 − 300 Da	2500 Da	3000 Da
Water permeability L/(h.bar.m^2)	1.95 ± 0.05	2.95 ± 0.05	6.40 ± 0.05

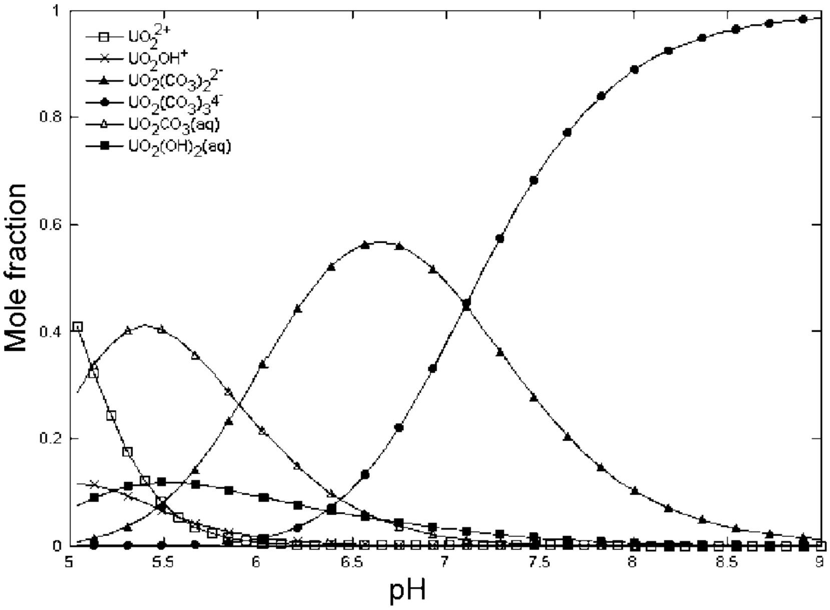

Figure 1. Distribution of uranium (VI) hydroxy and carbonate complexes as the function of the pH for $[UO^{2+}] = 1 \times 10^{-5}$ M, $[CO_3^{2-}] = 2 \times 10^{-3}$ M and [NaCl] = 0.19 M, T = 25°C build with CHESS software.

System from Spectro Analytical Instruments, ICP-AES) with a standard deviation of ± 2%. Analyte concentrations were determined with respect to calibration standards in dilute nitric acid. Absence of interferences was checked during the analysis. Seawater analysis was performed using an Inductively Coupled Plasma Mass Spectrometer (VARIAN, UltraMass700, ICP-MS). Analyte concentrations were determined using matrix-matched calibration. Na, K, Ca, and Mg are run under "cool plasma" conditions (plasma power reduced to 0.6–0.7 kW and nebulization gas increased to 0.9–1.0 mL/minute) in order to minimize argon polyatomics and eliminate isobaric interferences. The resolution was set at 0.8 amu at 5% of the peak.

RESULTS

Determination of the Membrane Selectivity

The measurements for all modules were performed in stable and identical conditions. Simulated seawater was filtered in cross-flow mode on membranes. The pH feed was kept constant at 8.3. Membrane performance

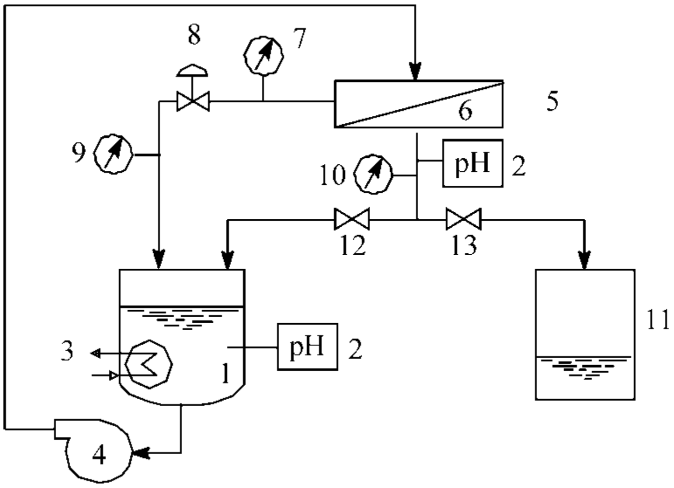

Figure 2. Schematic flow diagram of the lab-scale membrane system: 1, feed tank; 2. pH meter; 3, heat exchanger; 4, pump; 5, cell body; 6, membrane; 7, feed pressure gauge; 8, feed flow control valve; 9, retentate flux meter; 10, permeate flux meter; 11, permeate tank; 12 and 13, valves.

was measured in terms of uranium retention coefficient and U/Na$^+$ and U/Ca^{2+} selectivities (Fig. 3).

As expected, the membranes showed a high U(VI)/Na$^+$ and U(VI)/Ca^{2+} selectivity. Predictably, the highest cut-off membrane exhibits the lowest solute rejection for the same concentration. For the G20 membrane, the

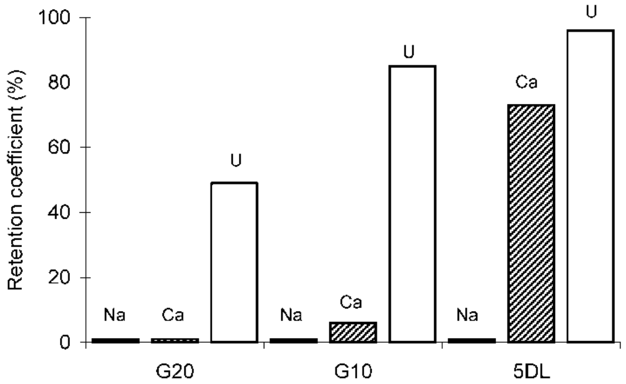

Figure 3. Retention coefficient of sodium, calcium and uranium as a function of the operating membrane; experimental conditions: T = 20°C, $\Delta P = 3$ bars, pH 8.3, $[UO_2^{2+}] = 1 \times 10^{-5}$ M, $[CO_3^{2-} + HCO_3^-] = 2 \times 10^{-3}$ M, $[NaCl] = 0.18$ M, and $[CaCl_2] = 9 \times 10^{-3}$ M.

rejection of uranium was 50%, while for G10 and 5DL membranes the retention coefficient of uranium was between 90 and 95% but U(VI)/Ca^{2+} selectivity of the 5DL membrane is dramatically low. Under those conditions, G10 membrane shows a high retention coefficient for U(VI) and a low retention coefficient for sodium and calcium, leading to high U(VI)/Ca^{2+} and U(VI)/Na^{+} selectivities.

Optimization of the Operating Parameters

The influence of the operating parameters on the retention coefficient of uranium was then studied with G10 membrane. The filtration tests were carried out according to transmembrane pressure (ΔP) varying from 2 to 5 bars and tangential velocity (J_r) varying from 40 to 140 mm s^{-1}. The temperature (20°C) and pH (8.3) were kept constant during the experiments. Samples of permeate and retentate were taken 45 min after each stage of operating parameters. The effect of applied pressure on U(VI) retention is reported in Fig. 4.

The U(VI) rejection decreases with pressure (ΔP), and increases when increasing tangential velocity (J_r). During membrane filtration, the U(VI) in the feed water is convectively driven to the membrane surface where it

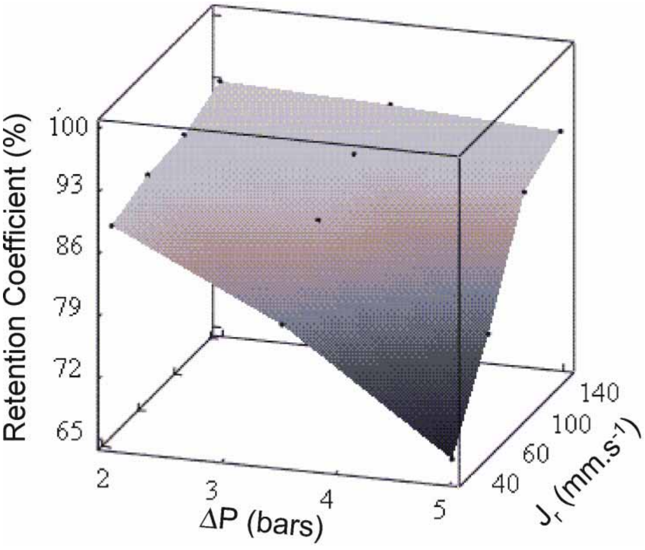

Figure 4. Retention coefficient of uranium as the function of the transmembrane pressure (ΔP) and tangential velocity (Jr). T = 20°C, pH 8.3, $[UO_2^{2+}] = 1 \times 10^{-5}$ M, $[CO_3^{2-} + HCO_3^{-}] = 2 \times 10^{-3}$ M.

builds a concentration polarization boundary layer near the membrane. This layer involves a reduction in charge density of the membrane and, consequently, attenuates the electrostatic repulsions between U(VI) in solution and the charges of the membranes (10) leading to a decrease of the rejection (11–13). The accumulation at the membrane surface is a function of the back transport of the complex to the bulk solution. To decrease the accumulation at the membrane surface, the tangential velocity (J_r) at the membrane surface is increased; complex retention thus increases.

Removal of Uranium from Seawater

The results obtained for the U(VI) rejection with simulated seawater prompted us to study the selective rejection of U(VI) from seawater. A concentration of 3.66 μg/L of uranium in prefiltrated seawater was determined by ICP-MS. The prefiltrated seawater was then diafiltrated with a transmembrane pressure (ΔP) of 3 bars and a tangential velocity (J_r) of 140 mm s^{-1}. The concentration of uranium in the retentate was then determined as a function of the nanofiltered volume ratio, and the results are displayed in Fig. 5.

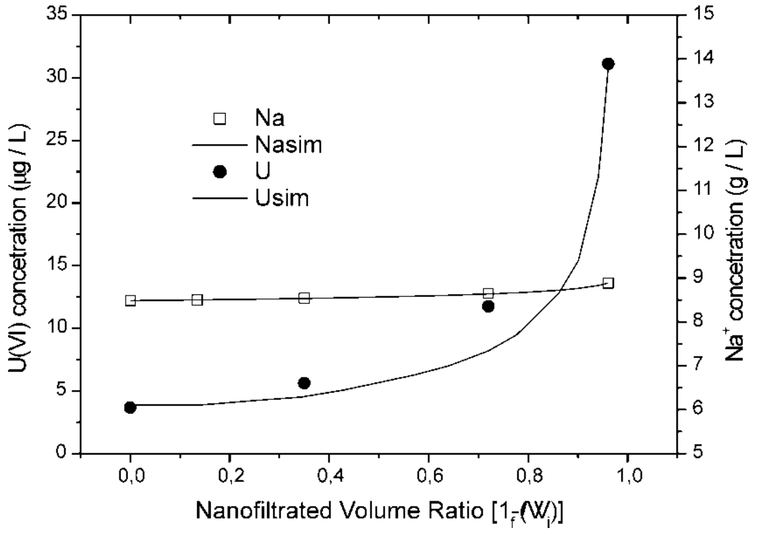

Figure 5. Concentration of Na^+ and U(VI) as a function of the nanofiltered volume ratio; experimental conditions: prefiltered seawater, T = 20°C, ΔP = 3 bars, G10 membrane; pH 8.3; J_r = 140 mm·s^{-1}. The filled circle and the square represent experimental data points and the solid line the theoretical fit of data with retention coefficient of 75% and 4% for uranium and sodium, respectively.

As expected, the concentration of U(VI) in the retentate is increased although sodium concentration is not affected by the dialfiltration process. The concentration of ions in the retentate may be expressed as a function of the nanofiltered volume ratio by Eq. (1).

$$C_f = C_i \times \left(\frac{V_f}{V_i}\right)^{RC} \tag{1}$$

where C_i and C_f are the initial and final concentration of metal ion, V_i and V_f are the initial and final volume, and RC the retention coefficient of metal ion. The fitting (least-squares method) of the theoretical curve obtained from Eq. (1) to the experimental data points leads to a retention coefficient of 75% and 3% for uranium and sodium, respectively.

The concentrations of the major seawater metal ions were determined before and after nanofiltration experiments for a nanofiltered volume ratio of 0.96 (Table 2).

The five major ions that occur at concentration down to 1 g/L are only slightly affected by the diafiltration process; the concentration factor is less than 1.5. Among the analyzed ions, only uranium and barium are concentrated, and they showed concentration factor of 8.5 and 10, respectively. As expected the bulky highly charged ions are rejected by nanofiltration membrane (14).

CONCLUSION

The objective of this study was to show the ability of nanofiltration to selectively reject uranium from seawater. With G10 membrane, uranium can be selectively concentrated by an 8.5 factor, and the concentration factor for

Table 2. Concentration and related concentration factor of the major seawater metal ions before and after diafiltration process with G10 membrane for a diafiltration volume ratio of 0.96 determined by ICP-MS

Elements	Initial concentration	Final concentration	%RSD	Conc. factor
Na	12200 mg/L	13600 mg/L	3.5	1.1
Mg	1420 mg/L	1800 mg/L	3.8	1.3
Ca	430 mg/L	565 mg/L	1.7	1.3
K	350 mg/L	413 mg/L	2.5	1.2
Sr	7.4 mg/L	9.8 mg/L	0.3	1.3
Li	0.3 mg/L	0.26 mg/L	3.1	0.9
Mo	0.1 mg/L	0.12 mg/L	0.3	1.2
Ba	0.014 mg/L	0.14 mg/L	1.5	10.0
U	3.66 μg/L	31.12 μg/L	1.6	8.5

the major metal ions dissolved in seawater is less than 1.5. Because of the weak uranium content of the sea (3.6 μg/L), the recovery of this element is difficult, and these results do not allow an economically viable process for the selective recovery of seawater uranium.

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