Supporting Information

Bare and polyelectrolyte-coated calcium carbonate particles for seawater uranium extraction: an eco-friendly alternative

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Summary

Synthesis of Calcium Carbonate Particles Coated with Poly(acrylic acid) (CaCO₃-PAA)

Synthesis of CaCO₃-PAA was performed in a 500 mL three-necks round bottom flask, under Argon flow and at a constant temperature of 30 °C. First, the precipitation of CaCO₃ was carried out by a double-jet injection method.[1] It consists of rapid and simultaneous injections of $CaCl_2$ aqueous solution (11 mL at 0.1 M, pH = 8.6 adjusted with NH_3) and $(NH_4)_2CO_3$ aqueous solution (11 mL at 0.1 M, pH = 9.9 adjusted with NH_3) into water (378 mL, pH = 8.5 adjusted with NH_3) under strong stirring (magnetic stirrer set at 1500 rpm). Second and still at T = 30 °C and under strong stirring (1500 rpm), aqueous solution of PAA (126 µL at 0.1 M, pH ≈ 8) was injected in the reaction 60 s after the double-jet injection of $CaCl_2$ and $(NH_4)_2CO_3$ (delayed addition of PAA). In these conditions, $[Ca^{2+}]$ = 2.75 mM and the ratio of carboxylate groups and Ca^{2+} cations is $[COO^-]/[Ca^{2+}]$ = 0.62. After 2 h, the product (CaCO₃-PAA particles) was isolated by vacuum filtration (using 220 nm cut-off filtration membrane), washed 3 times with 200 mL of water and immediately dried in vacuum oven at 60 °C for 1 h.

Synthesis of Calcium Carbonate Particles Coated with Poly(ethyleneimine) (CaCO₃-PEI)

CaCO₃-PEI were prepared according to the following protocol: typically, 19.2 mg of CaCO₃-PAA particles (synthesized with a delayed addition of PAA of 60 s) were dispersed in 17 mL of water and sonicated for 3 min. pH of the dispersion was 8.5. A 4.2 mM aqueous solution of PEI (1.428 g of PEI into 85 mL of water) was prepared and its pH decreased from 11.3 to 8.6 by addition of HCl. CaCO₃-PAA dispersion was then added dropwise to PEI solution under strong stirring at room temperature. After 2 h of reaction, CaCO₃-PEI particles were purified from excess of PEI by dialysis (for 2 h, *versus* 2 L of water at pH = 8.5 (NaOH), 4 times). Then, solvent was evaporated under reduced pressure at T = 50 °C. Finally, CaCO₃-PEI particles were dried in vacuum oven at 60 °C for 1 h.

Preparation of Artificial Seawater

Artificial seawater was prepared according to the "Standard Practice for the Preparation of Substitute Ocean Water – ASTM D1141-98(2013)".[2] Additionally, trace elements Zn, V and Mo which are naturally present in seawater but absent from to the standard ASTM D1141-98 composition were added through zinc chloride, divanadium pentaoxide and molybdenum(VI) oxide with final concentrations [Zn] = 3.5 ppb, [V] = 1.8 ppb and [Mo] = 3.8 ppb.

Artificial seawater was prepared as follow: in a graduated bottle, salts were introduced sequentially into 850 mL of stirred deionized water in the order they appear in the Table S1. Then, deionized water was added to reach a volume of 1 L. 10 minutes after preparation, the artificial seawater looks transparent and no precipitate was observed. pH is 7.8. The artificial seawater was stored in a dark place at T = 4 °C and filtered with 200 nm cut-off membrane Acrodisc® syringe filter prior to use. Fresh artificial seawater was prepared regularly all along the duration of the study.

Table S1 - Artificial seawater composition. Names, chemical formulas and masses of the salts sequentially introduced in pure water during the preparation of 1 L of artificial seawater. Final concentration in salts in the as-prepared artificial seawater are presented in the last column of the table.

Salt	Chemical formula	Mass (g)	Final concentration (g L^{-1})
Sodium chloride	NaCl	24.53	24.53
Magnesium chloride hexahydrate	$MgCl_2$, 6 H_2O	11.103	11.103
Sodium sulfate	Na_2SO_4	4.09	4.09
Calcium chloride dehydrate	$CaCl_2$, 2 H_2O	1.536	1.536
Potassium chloride	KCl	0.695	0.695
Sodium bicarbonate	$NaHCO_3$	0.201	0.201
Potassium bromide	KBr	0.101	0.101
Boric acid	H_3BO_3	0.027	0.027
Strontium chloride hexahydrate	$SrCl_2$, 6 H_2O	0.004	0.004
Sodium fluoride	NaF	0.003	0.003
Zinc chloride	$ZnCl_2$	7.3×10^{-6}	7.3×10^{-6}
Divanadium pentaoxide	V_2O_5	3.21×10^{-6}	3.21×10^{-6}
Molybdenum(VI) oxide	MoO_3	1.17×10^{-5}	1.17×10^{-5}

Dynamic Light Scattering (DLS) and Zeta Potential Measurements: Experimental Methods

DLS and Zeta potential (ξ_p) measurements were made at T = 25 °C with a NanoBrook Omni instrument. For DLS, the wavelength of the light source was λ = 632.8 nm and the scattering angle θ = 90°. Collective diffusion coefficients D were obtained from interpretations of the autocorrelation functions of the scattered light using both the method of 2nd order cumulants and the CONTIN fitting procedure provided by the instrument software. Hydrodynamic diameters (D_H) were calculated according to the Stokes-Einstein relation, $D_H = k_B T/3\pi\eta D$, where k_B is the Boltzmann constant, T the temperature and η the solvent viscosity (0.89 mPa s for water and 0.94 mPa s for seawater at 25 °C).

Incubation of Particles in Artificial Seawater and Characterization of Uranium and other Elements Extractions: Experimental Details

$CaCO_3$, $CaCO_3$-PAA and $CaCO_3$-PAA-PEI particle dispersions in artificial seawater containing various concentrations were prepared as follow: first, a uranium stock solution at [U] = 2 g L^{-1} was prepared by dissolving 210.9 mg of $UO_2(NO_3)_2 \cdot 6\,H_2O$ in 50 mL of DIW. pH of the solution was increased from 3.3 to 7.8 with NaOH. Then, solutions at [U] = 0.2, 0.02 and 0.002 g L^{-1} were prepared by dilution in water. Second, $CaCO_3$, $CaCO_3$-PAA and $CaCO_3$-PAA-PEI dispersions at 6.2 mg mL^{-1} were prepared by adding dry powders in deionized water. Dispersions were stirred for 24 h and the non-aggregated state of the particles was checked by DLS analysis. Third, artificial seawater was prepared following the procedure given in the section "Preparation of artificial seawater" of this document, excepted that the process was stopped before the last step (completion to 1 L by addition of deionized water). Thus, 858 mL of "concentrated artificial seawater" was obtained with a concentration factor of 1.165 compared to the "standard" artificial seawater. Fourth, uranium solution and particles dispersions were introduced in various amount in the "concentrated artificial seawater" in order to create mixtures at [particle] = 0.95 mg mL^{-1} and [U]$_0$ = 2.8 , 52.8, 102.8, 1002.8 and 10002.8 ppb in a seawater-like media containing > 98 % of the salts contained in the "standard" artificial seawater. Samples compositions are detailed in Table S2. Volumes or corresponding masses were respectively measured with micropipettes and a microbalance.

Table S2 - Compositions and characteristics of $CaCO_3$, $CaCO_3$-PAA and $CaCO_3$-PAA-PEI particle dispersions in artificial seawater containing various concentrations of uranium. Columns labelled "Preparation" gives information about the 3 components mixed to create the samples while columns labelled "Sample" gives information about the samples.

	Preparation			Sample			
	V of particle dispersion in water at 6.2 mg mL^{-1} (mL)	V (mL) and concentration (g L^{-1}) of uranium solution in water	V of "concentrated seawater" (mL)	Uranium concentration $[U]_0$ (ppb)	Particle concentration (mg mL^{-1})	Concentration of salts compared to artificial seawater (%)	Total volume (mL)
$CaCO_3$ with 2.8 ppb of U	1.839	0.0168 at 0.002	10.144	2.8	0.95	98.48	12
$CaCO_3$ with 52.8 ppb of U	0.306	0.0053 at 0.02	1.689	52.8	0.95	98.33	2
$CaCO_3$ with 102.8 ppb of U	0.306	0.0103 at 0.02	1.683	102.8	0.95	98.04	2
$CaCO_3$ with 1002.8 ppb of U	0.306	0.0100 at 0.2	1.683	1002.8	0.95	98.06	2
$CaCO_3$ with 10002.8 ppb of U	0.306	0.0100 at 2	1.684	10002.8	0.95	98.06	2
$CaCO_3$-PAA with 2.8 ppb of U	1.839	0.0168 at 0.002	10.144	2.8	0.95	98.48	12
$CaCO_3$-PAA with 52.8 ppb of U	0.306	0.0053 at 0.02	1.689	52.8	0.95	98.33	2
$CaCO_3$-PAA with 102.8 ppb of U	0.306	0.0103 at 0.02	1.683	102.8	0.95	98.04	2
$CaCO_3$-PAA with 1002.8 ppb of U	0.306	0.100 at 0.2	1.683	1002.8	0.95	98.06	2
$CaCO_3$-PAA with 10002.8 ppb of U	0.306	0.100 at 2	1.683	10002.8	0.95	98.06	2
$CaCO_3$-PEI with 2.8 ppb of U	1.839	0.0168	10.144	2.8	0.95	98.48	12
$CaCO_3$-PEI with 52.8 ppb of U	0.306	0.0053 at 0.02	1.689	52.8	0.95	98.33	2
$CaCO_3$-PEI with 102.8 ppb of U	0.306	0.0103 at 0.02	1.683	102.8	0.95	98.04	2
$CaCO_3$-PEI with 1002.8 ppb of U	0.306	0.100 at 0.2	1.683	1002.8	0.95	98.06	2
$CaCO_3$-PEI with 10002.8 ppb of U	0.306	0.100 at 2	1.683	10002.8	0.95	98.06	2

SEM Images and Size Distribution of CaCO₃, CaCO₃-PAA and CaCO₃-PEI

Representative SEM images of $CaCO_3$, $CaCO_3$ and $CaCO_3$-PEI particles are presented in Fig. S1a, S1b and S1c, respectively. The probability distribution functions of size of each type of particles were established from series of images similar to that of Fig. S1a, S1b and S1c. The probability distribution functions of size are presented in Fig. S1a',S1b' and S1c'. The data are fitted using a Log-Normal function (equation S1):

$$p(D) = \frac{1}{\sqrt{2\pi} \times s_0 \times D} \, exp\left(-\frac{ln^2(D/D_0)}{2 \times s_0^2}\right) \qquad \text{(S1),}$$

where D_0 is the median diameter of the distribution and s_0 its polydispersity index.
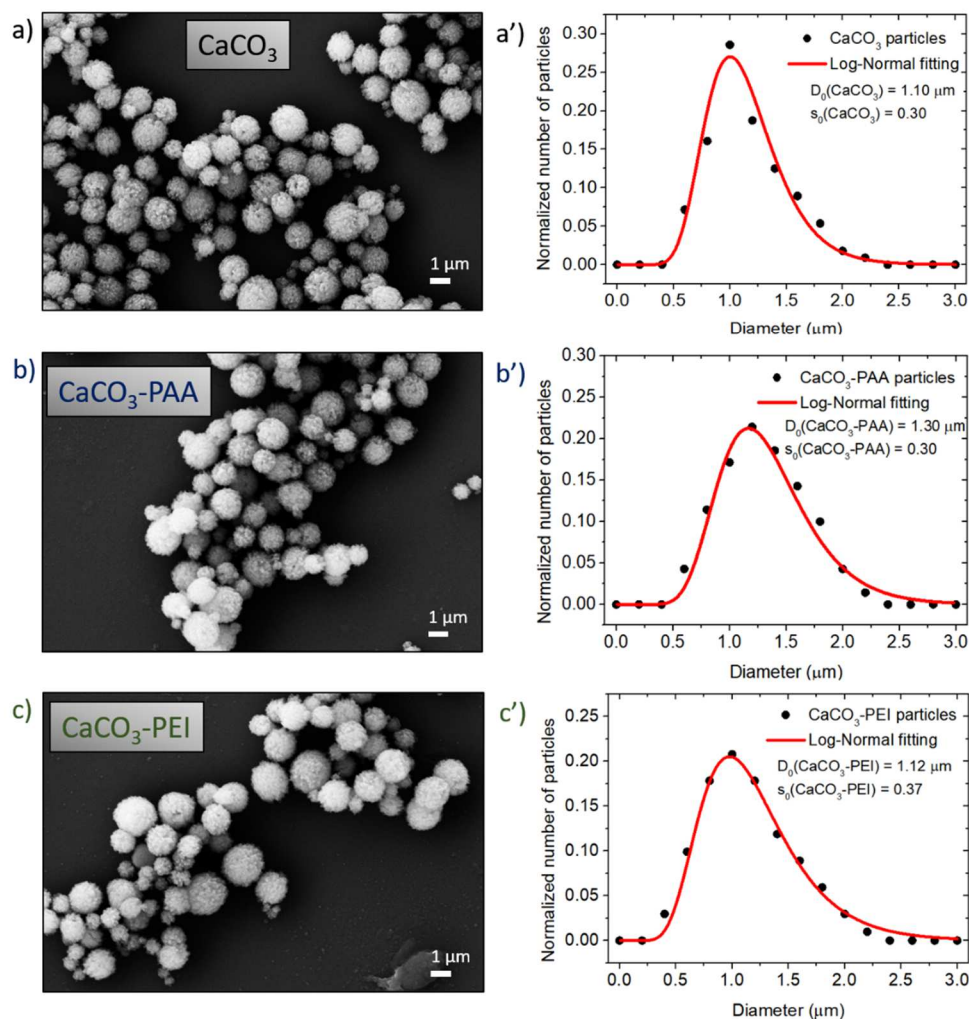

Fig. S1 - SEM images and corresponding size distributions of $CaCO_3$ (a and a'), $CaCO_3$-PAA (b and b') and $CaCO_3$-PEI (c and c') particles. Median diameters D_0 and polydispersity indexes s_0 are extracted from Log-Normal fittings of the data.

XRD Analysis of the Bare CaCO₃ Particles

       Fig. S2 displays the X-ray diffraction pattern (XRD) of the bare $CaCO_3$ particle sample in powder. "Material Analysis Using Diffraction" (MAUD) software has been used to determine allotropic fraction in the calcium carbonate sample. The sample mainly contains vaterite ($\approx$ 98 %), as evidenced by the strong diffraction peaks at 2θ = 25 °, 27 ° and 33 °, and a small fraction of calcite ($\approx$ 2 %) identified by the diffraction peak at 2θ = 29.5 °. For comparison, please see JCPDS references for vaterite (#033–0268) and calcite (#005–0586). The peak at 2θ = 36 ° is attributed to the presence of NaCl as impurity.
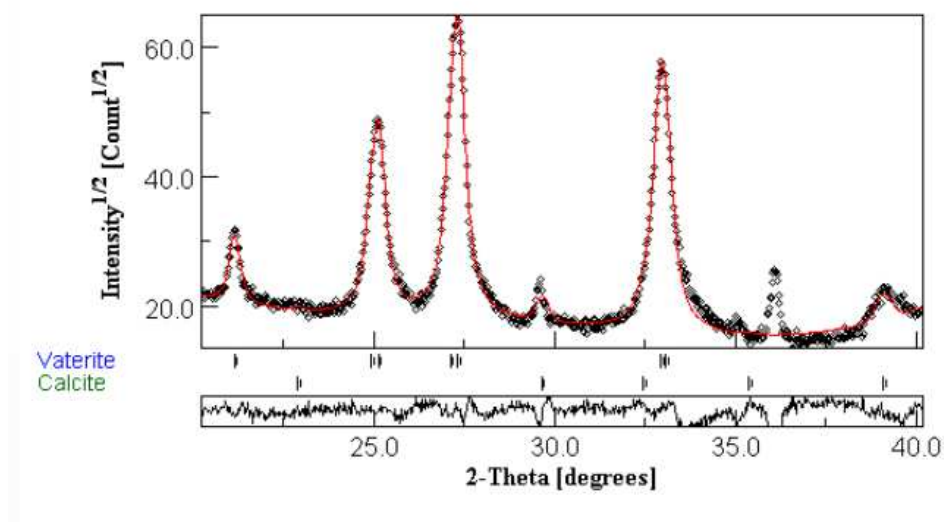

Fig. S2 - XRD pattern of the bare $CaCO_3$ particles. Raw data (black) and calculation using MAUD software (red). Analysis reveals that the sample is made of 98 % of vaterite and 2 % of calcite.

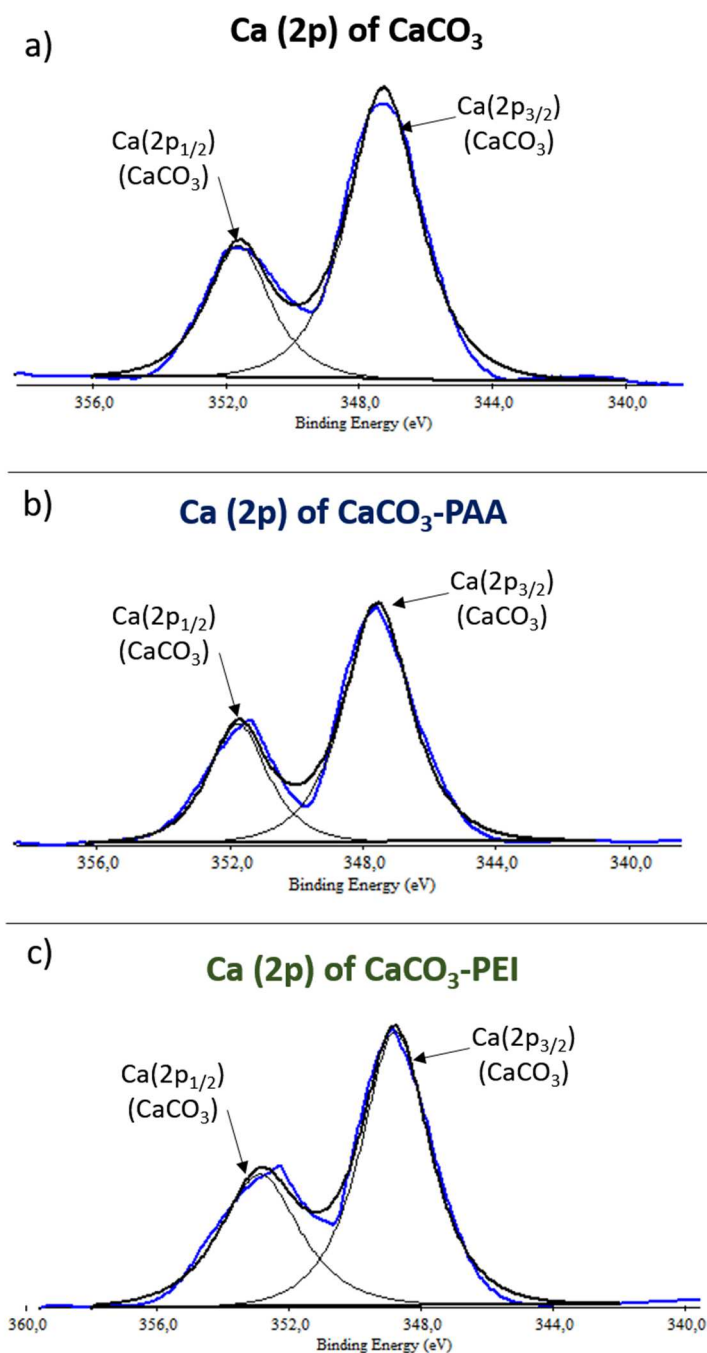# XPS Analysis of the Ca (2p) peak of CaCO₃, CaCO₃-PAA and CaCO₃-PEI

Fig. S3 - XPS Ca (2p) core level spectra of CaCO$_3$ (a), CaCO$_3$-PAA (b) and CaCO$_3$-PEI (c) with a two-peak fits corresponding to Ca (2p$_{1/2}$) and Ca (2p$_{3/2}$) binding energies of calcium carbonate.

Synthesis of CaCO₃-PAA: Effect of the Delay of PAA Addition on Size and Structure of the Particles

In this section, CaCO₃-PAA particles were synthesized according to the protocol described in part 2.2 of the article and in the section "Synthesis of Calcium Carbonate Particles Coated with Poly(acrylic acid) (CaCO₃-PAA)" of this document, excepted that aqueous solution of PAA (126 µL at 0.1 M, pH ≈ 8) was injected in the reaction bath either 5, 15, 30, 45 or 60 s after the double-jet injection of $CaCl_2$ and $(NH_4)_2CO_3$. The as-prepared particles were purified by dialysis (for 2 h, *versus* 2 L of water at pH = 8.5 (NaOH), 4 times) instead of vacuum filtration.

Fig. S4 shows D_H of the particles after purification according to duration of the delay of PAA addition.
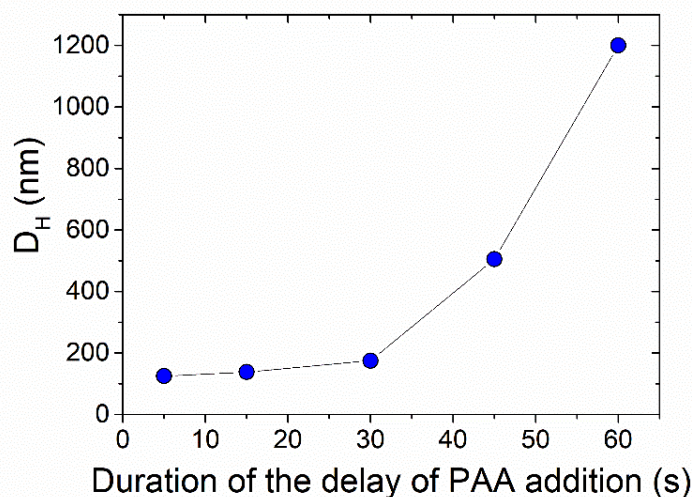

Fig. S4 - Hydrodynamic diameters D_H of CaCO₃-PAA as a function of the duration of the delay of the PAA addition during synthesis.

CaCO₃-PAA particles synthesized with delayed additions of PAA of 5, 15, 30 and 45 s are not colloidally stable in water at pH = 8.5 (NH₃). For all of these samples, precipitations were observed in the few days following the syntheses. CaCO₃-PAA particles synthesized with delayed addition of PAA of 60 s show remarkable colloidal stability over weeks with constant value of D_H in similar conditions.

CaCO₃-PAA particles synthesized with delayed addition of PAA of 45 s and 60 s were spread on glass slides immediately after purification, dried and analyzed by XRD. Fig. S5a and S5b show the XRD patterns of the respective samples.

The XRD pattern of the CaCO₃-PAA particles synthesized with delayed addition of PAA of 45 s (Fig. S5a) does not show diffraction peaks excepted at 2θ = 31.73 °. It is deduced from that pattern and from literature that the particles are amorphous.[3] By contrast, the XRD pattern of the CaCO₃-PAA particles synthesized with delayed addition of PAA of 60 s (Fig. S5b) presents diffraction peaks corresponding to vaterite structure (standard card : #033-0268). The 2θ peaks at 24.9°, 27.04°, 32.78°, 43.85° and 50.08° correspond to hkl plans 110, 112, 114, 300 and 118, respectively.
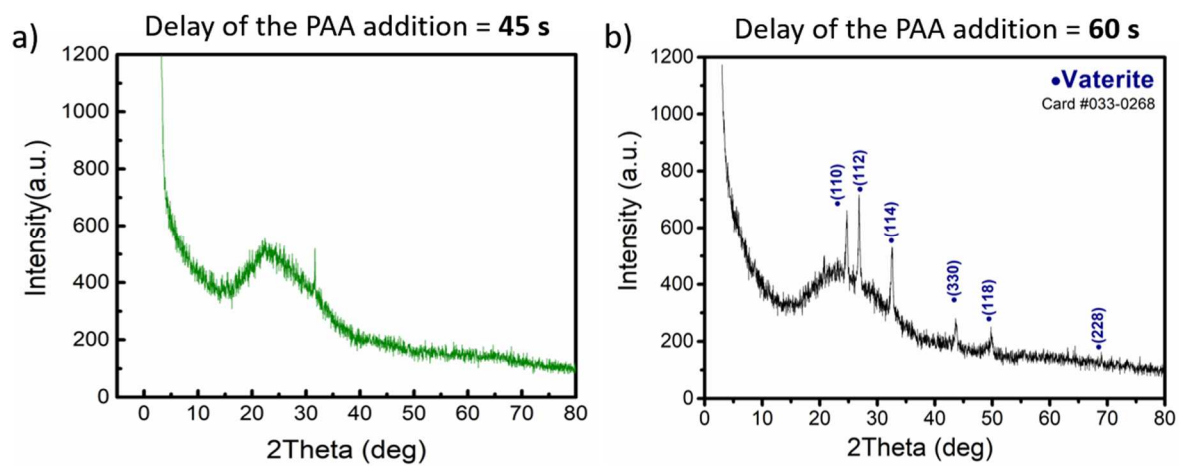
Fig. S5 - XRD patterns (on glass slides) of CaCO$_3$-PAA particles synthesized with delayed addition of PAA of 45 s (a) and 60 s (b) revealing amorphous (a) and vaterite (b) structures.

TGA: Thermogravimetric Analysis of CaCO₃, CaCO₃-PAA and CaCO₃-PEI

Thermogravimetric (TGA) experiments were performed on the 3 types of particles. Weight losses of $CaCO_3$ (black curve), $CaCO_3$-PAA (blue curve) and $CaCO_3$-PEI (green curve) particles according to temperature are presented in Fig. S6.
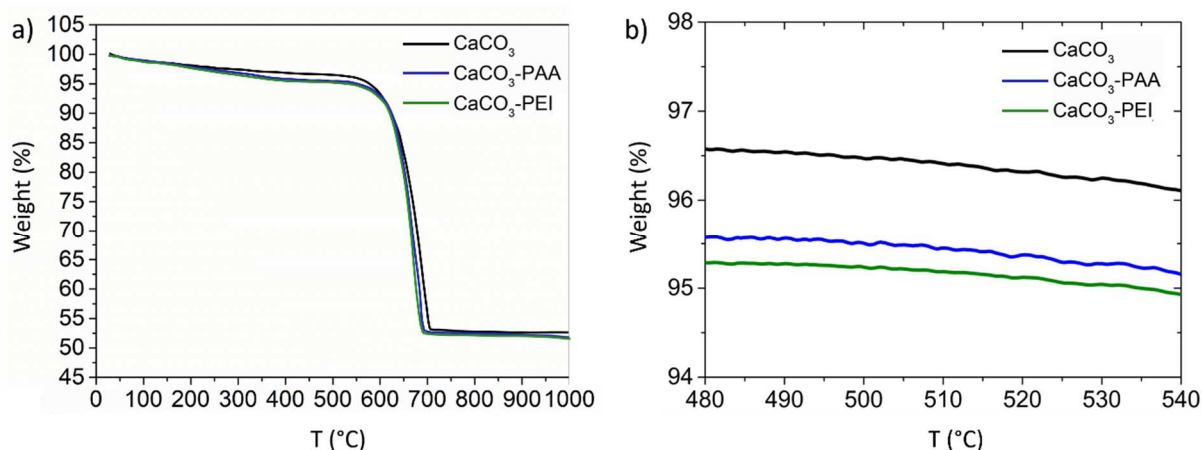

Fig. S6 – a) Thermogravimetric analysis (TGA): weight loss (%) *versus* temperature (°C) for the thermal decomposition of $CaCO_3$ (black curve), $CaCO_3$-PAA (blue curve) and $CaCO_3$-PEI (green curve). b) Zoom of the region around $T = 515$ °C.

On the one hand, organic polyelectrolytes such as PAA and PEI are thermally decomposed between 175 °C and 500 °C, with an overall weight loss of 86 %.[4] On the other hand, calcium carbonate thermal decomposition into CO_2 and CaO occurs between 635 °C and 865 °C with an overall weight loss of 44 %.[5,6] Thus and theoretically, at 500 °C $\leq T \leq$ 635 °C, no overlap should exist between thermal degradations of PAA and PEI and thermal degradation $CaCO_3$. Weight percentages of PAA in $CaCO_3$-PAA, and PAA and PEI $CaCO_3$-PEI were then calculated from weight losses at $T = 515$ °C by: a) for $CaCO_3$-PAA: subtracting the weight percentage of $CaCO_3$ at 515 °C to the weight percentage of $CaCO_3$–PAA at 515 °C; b) for $CaCO_3$-PEI: subtracting the weight percentage of $CaCO_3$-PAA at 515 °C to the weight percentage of $CaCO_3$–PEI at 515 °C; and c) multiplying the obtained values by a factor $100/86$ (considering overall weight loss of 86 % for these polymers). Results give $m_{(PAA)} = 1.09$ % for $CaCO_3$–PAA and $m_{(PEI)} = 0.30$ % for $CaCO_3$–PEI. The total mass of polyelectrolytes in $CaCO_3$–PEI is calculated as $m_{(PAA+PEI)} = m_{(PAA)} + m_{(PEI)} = 1.39$ %.

Precipitation of Uranium Species in Artificial Seawater

In this study, the aim is to only focus on interactions between sorbents and soluble uranium species to fit to real oceanic conditions where uranium precipitates would drop down. It is also important to avoid misinterpretations due to imperfect separation between calcium carbonate particles and insoluble uranium during purification steps. We therefore prepared artificial seawater batches with increasing concentrations of uranium and analyzed them by DLS over time in order to determine below which concentration uranium remains soluble.

Artificial seawater batches containing 10 ppm, 50 ppm, 100 ppm and 1000 ppm of uranium were prepared. First, a uranium stock solution at [U] = 2 g L^{-1} was prepared by solubilizing 210.9 mg of $UO_2(NO_3)_2 \cdot 6H_2O$ in 50 g of deionized water. pH was rapidly increased from 4.3 to 7.8 by addition of 3M NaOH. Uranyl nitrate was quickly dissolved. The yellowish solution was stirred for 15 min. The $UO_2(NO_3)_2$ solution was analyzed by DLS and no particles were detected (D_H = 0 nm). Second and immediately after the stirring period, 0.015 mL, 0.075 mL, 0.15 mL and 1.5 mL of uranyl nitrate solution at [U] = 2 g L^{-1} were mixed with 2.985 mL, 2.925 mL, 2.85 mL and 1.5 mL of filtered (200 nm cut-off polysulfone membrane) artificial seawater, giving mixtures at [U] = 10 ppm, 50 ppm, 100 ppm and 1000 ppm, respectively. pH of the mixtures is 7.8. The mixtures (seawater at [U] = 10 ppm, 50 ppm, 100 ppm and 1000 ppm) were then analyzed by DLS 10 min, 1 h and 24 h after their preparation. Table S3 presents D_H measurements and observations regarding stability or phase separation.

Table S3 - Hydrodynamic diameters (D_H, nm) measurements of samples of seawater containing 10 ppm, 50 ppm, 100 ppm and 1000 ppm of uranium. Measurements were made 10 min, 1 h and 24 h after preparation (i. e. introduction of uranyl nitrate solution in seawater). pH of all the samples is 7.8.

	[U] = 10 ppm	[U] = 50 ppm	[U] = 100 ppm	[U] = 1000 ppm
t = 10 min	0 nm	0 nm	0 nm	0 nm
t = 1 h	0 nm	0 nm	≈ 300 nm (unstable colloidal system)	> 5000 nm (precipitation)
t = 24 h	0 nm	0 nm	> 4000 nm (precipitation)	> 5000 nm (precipitation)

EDX Analysis of CaCO$_3$, CaCO$_3$-PAA and CaCO$_3$-PEI

Our first intention was to analyze particles by EDX spectroscopy after incubation at concentrations ≤ 10 ppm. Unfortunately, our instrument was not sensitive enough to detect uranium after adsorption at such concentrations. Particles were therefore incubated 3 times (3 × 10 min, 3 × 1 h and 3 × 48 h) in seawater containing 50 ppm of uranium, which is the highest concentration without any insoluble uranium detectable by DLS (see "DLS study of the formation of uranium-based precipitate in seawater according to uranium concentration" in this document).
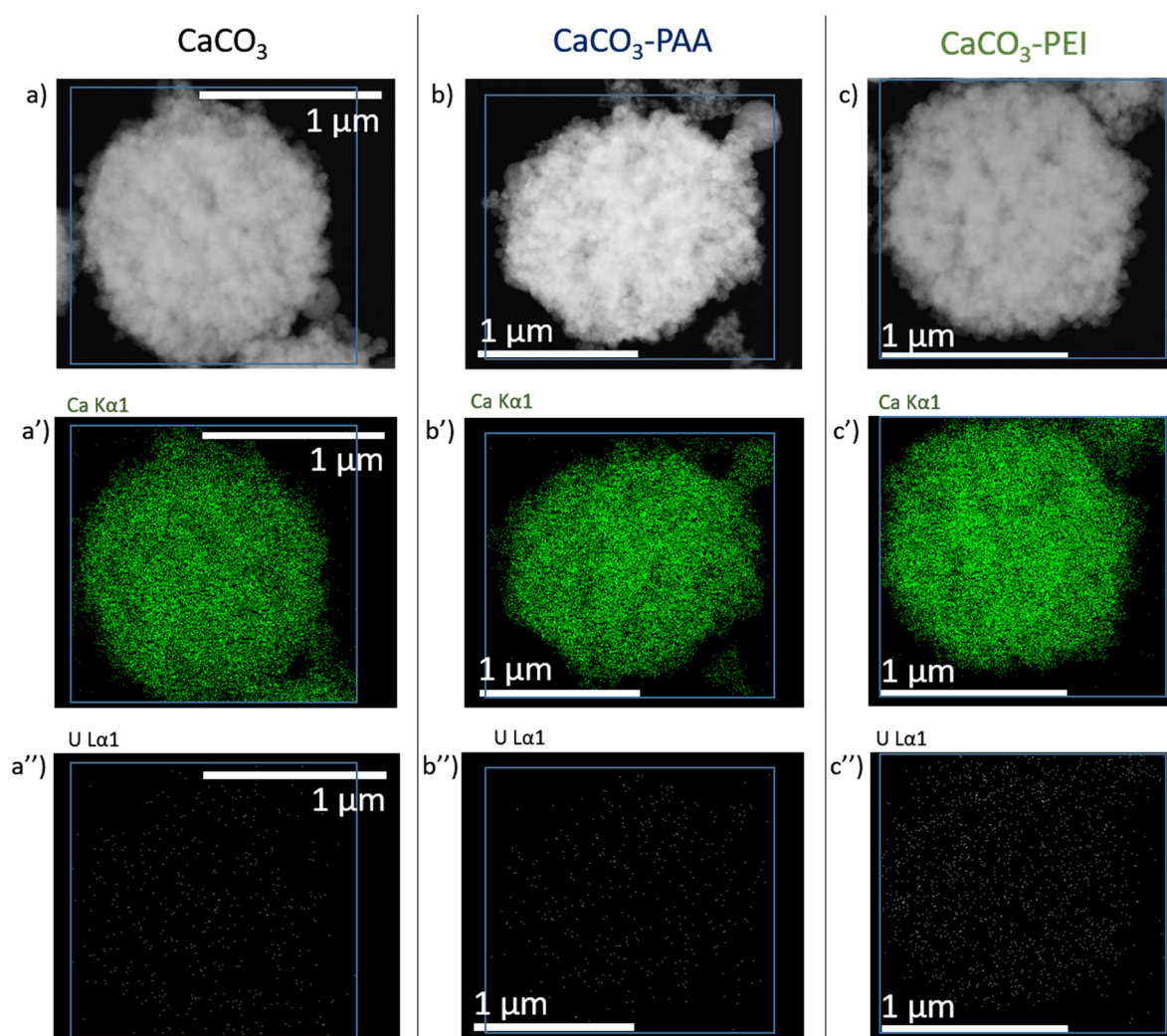

Fig. S7 - TEM images (a, b and c) and corresponding Ca (a', b' and c') and U (a'', b'' and c'') EDX mapping images of CaCO$_3$ (a, a' and a''), CaCO$_3$-PAA (b, b' and b'') and CaCO$_3$-PEI (c, c' and c'') particles after incubation in seawater containing 50 ppm of uranium for 144 h (48 h of incubation followed by purification, repeated 3 times). Blue lines delimitate the areas in which EDX scans were performed.

CaCO$_3$, CaCO$_3$-PAA and CaCO$_3$-PEI particles were first dispersed in water at 2.85 mg mL^{-1}. pH were then adjusted to 7.5 and dispersions stirred for 15 min. Uranyl nitrate solution at 2 mg mL^{-1} in water was prepared and its pH increased to 5.5. Then, 1.333 mL of particles dispersions and 0.1 mL of uranium solution were added to 2.567 mL of artificial seawater, giving mixtures at [particle] = 0.95 mg mL^{-1} and [U] = 50 ppm. pH were adjusted to 7.8. Mixtures were stored at 25 °C on a shaking plate at 55 rpm for incubation periods of 10 min, 1 h and 48 h. After incubation, particles were purified by 4 cycles of centrifugation (10,000 rpm, 10 mins) and addition of seawater. Then supernatant was remove and particles dried in oven at 60 °C. The dried particles (loaded with uranium) were then used to prepared new mixture in seawater containing 50 ppm of U, kept for 10 min, 1 h and 48 h respectively, then purified and dried again as described before. The whole processes were repeated 3 times for total incubations times of 30 min, 3 h and 144 h. Colloidal stability was checked by DLS at the end of each incubation period before particles were purified.
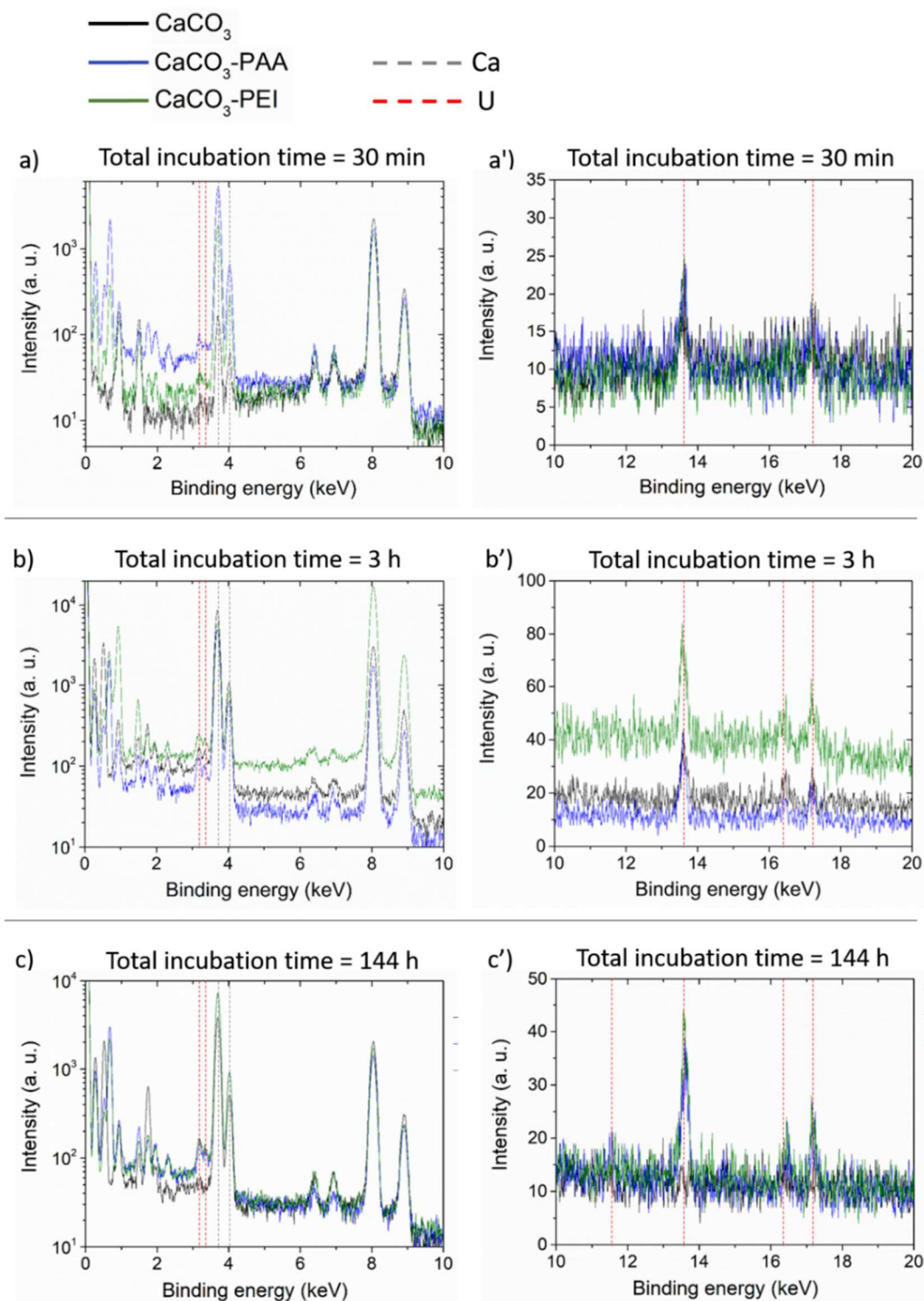
Fig. S8 - Electron dispersive X-ray (EDX) spectra of $CaCO_3$ (black lines), $CaCO_3$-PAA (blue lines) and $CaCO_3$-PEI (green lines) after incubation at 25 °C in seawater containing 50 ppm of uranium for total times of 30 min (10 min of incubation followed by purification, repeated 3 times, a and a'), 3 h (1 h of incubation followed by purification, repeated 3 times, b and b') and 144 h (48 h of incubation followed by purification, repeated 3 times, c and c'). For each incubation time: EDX spectrum is presented in a couple of Figures with different intensity scales: a, b and c from 0 to 10 keV and a', b' and c' from 10 to 20 keV. Dashed grey and red vertical lines indicate positions of easily identifiable peaks of respectively calcium and uranium.

15

XPS analysis of CaCO₃, CaCO₃-PAA and CaCO₃-PEI incubated with uranium

Experimental procedure: CaCO₃, CaCO₃-PAA and CaCO₃-PEI particles were incubated with uranium with the aim to analyze the obtained uranium-loaded particles by XPS. A first series of CaCO₃, CaCO₃-PAA and CaCO₃-PEI was incubated with uranium in seawater, and a second series incubated with uranium in deionized water with pH adjusted to 7.8 with a tiny amount of NaOH.

CaCO₃, CaCO₃-PAA and CaCO₃-PEI particles were first dispersed in seawater or water at 2.85 mg mL^{-1}. pH were then adjusted to 7.5 and dispersions stirred for 15 min. Uranyl nitrate solution at 2 mg mL^{-1} in water was prepared and its pH increased to 5.5. Then, 1.32 mL of Uranyl nitrate solution at 2 mg mL^{-1} was added to mixtures of 17.54 mL of particles at 2.85 mg mL^{-1} and 33.89 mL of seawater or water, giving mixtures at [particle] = 0.95 mg mL^{-1} and [U] = 50 ppm. These mixtures of particles and uranium were incubated at 25 °C on a shaking plate set at 55 rpm for 10 min. Then, mixtures were centrifuged at 10000 rpm for 6 min. Supernatants were removed and replaced by 35 mL of seawater or water. Samples were shaken, centrifuged again and supernatants were removed. After that, particles were re-incubated with 50 ppm of uranium and purified again, for a total of 3 incubation with 50 ppb uranium solutions. Finally, all samples were purified by addition of seawater or water and centrifugation (3 times) and dried at 50 °C in vacuum oven. Powder samples were then analyzed by XPS.
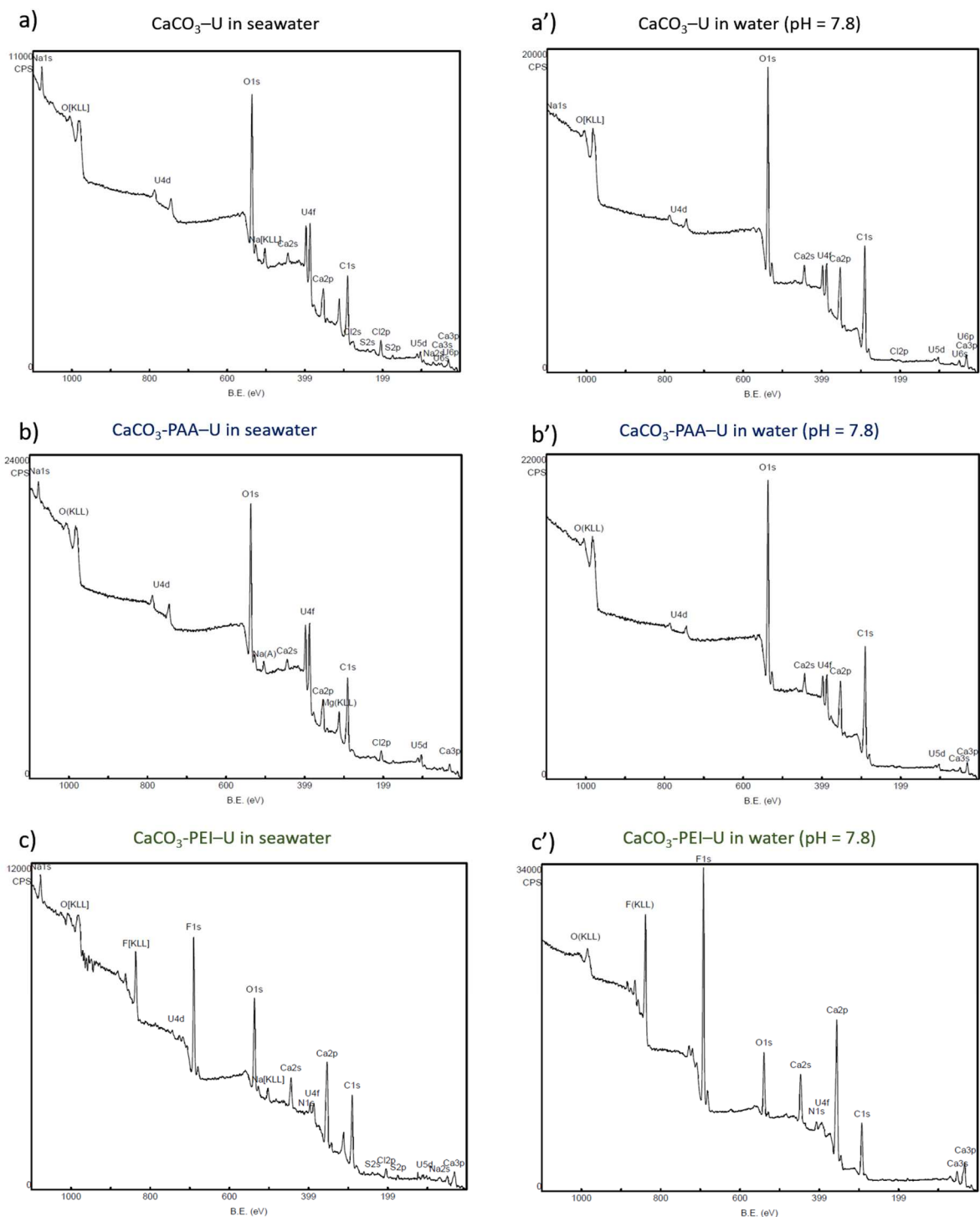
Fig. S9 – XPS survey spectra of CaCO$_3$ (a and a'), CaCO$_3$-PAA (b and b'), and CaCO$_3$-PEI (c and c') after 3 cycles of incubation and purification with 50 ppb of uranium in seawater (a, b and c) and water at pH = 7,8 (a', b' and c'). U(4f) peak, centered at 387.5 eV, is visible on all spectra.
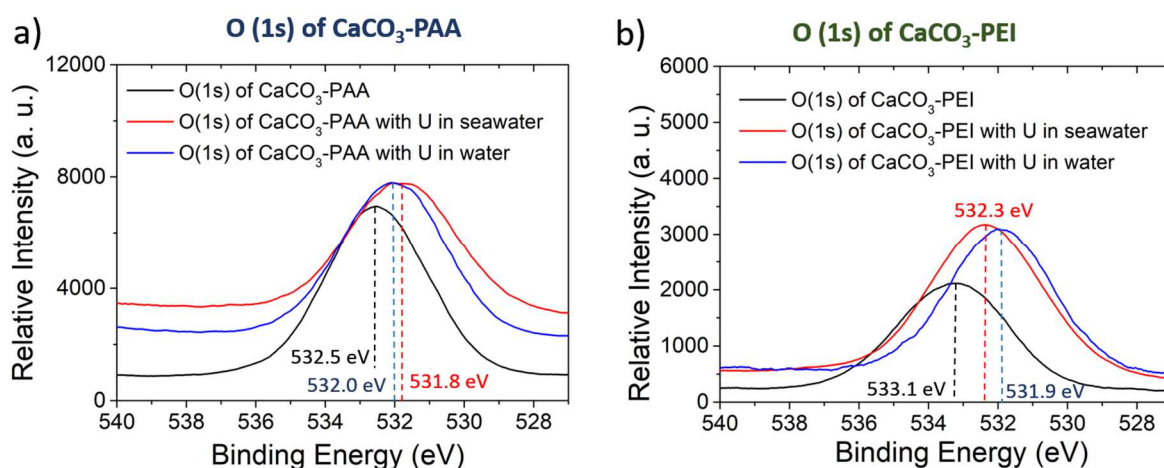
Fig. S10 - O(1s) XPS spectra of CaCO$_3$-PAA (a) and CaCO$_3$-PEI (b) particles before and after incubation with uranium in seawater and water at pH = 7.8.

Desorption and reusability studies

Experimental procedure: First, CaCO$_3$-PAA and CaCO$_3$-PEI at 0.95 mg mL^{-1} were incubated at T = 25 °C and for 24 h in seawater containing 1002.8 ppb of uranium (see Materials and Methods, part 2.5). Then, particles were isolated by ultrafiltration, washed 3 times by addition of seawater and ultrafiltration, and dried in vacuum oven at T = 50 °C. Second, the uranium-loaded particles were redispersed in pure water and desorbing agent solutions (NaOH, Na$_2$EDTA, NaHCO$_3$ and Na$_2$SO$_4$) at 0.1 mol L^{-1} as concentration in particles was 0.05 mg mL^{-1} (typically 5 mg of particles in 100 mL of solution). After incubation periods of 0.5 h and 24 h, particles were isolated by centrifugation (10000 rpm, 10 min). Supernatants, containing desorbed uranium species, were collected and filtered (400 nm cut-off polyethersulfone membranes) in order to separate dissolved uranium species and uranium-based nanoparticles (potentially existing at high pH and low U concentration) from remaining calcium carbonate particles. The filtered supernatants were then concentrated by evaporation under reduced pressure and their concentrations in uranium determined by ICP. The mass fractions of desorbed uranium (in mg of U per g of particles) were deducted from the ICP measurements. Finally, the desorption rates (in %) were calculated as the ratio between the mass fraction of desorbed uranium and the mass fraction of formerly adsorbed uranium (using the $Q_e^{particles\,(ICP)}$ values presented in Fig. 5c).

For the adsorption-desorption cycles experiments, the particles which have been isolated by centrifugation after incubation with desorbing agent solutions were washed twice by addition of water at pH = 7.8 (NaOH) and ultrafiltration, and then dried before being reused for uranium adsorption in seawater.

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