

Carbonate effects on hexavalent uranium removal from water by nanocrystalline titanium dioxide

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Abstract

A novel nanocrystalline titanium dioxide was used to treat depleted uranium (DU)-contaminated water under neutral and alkaline conditions. The novel material had a total surface area of 329 m²/g, total surface site density of 11.0 sites/nm², total pore volume of 0.415 cm³/g and crystallite size of 6.0 nm. It was used in batch tests to remove U(VI) from synthetic solutions and contaminated water. However, the capacity of the nanocrystalline titanium dioxide to remove U(VI) from water decreased in the presence of inorganic carbonate at pH > 6.0. Adsorption isotherms, Fourier transform infrared (FTIR) spectroscopy, and surface charge measurements were used to investigate the causes of the reduced capacity. The surface charge and the FTIR measurements suggested that the adsorbed U(VI) species was not complexed with carbonate at neutral pH values. The decreased capacity of titanium dioxide to remove U(VI) from water in the presence of carbonate at neutral to alkaline pH values was attributed to the aqueous complexation of U(VI) by inorganic carbonate. The nanocrystalline titanium dioxide had four times the capacity of commercially available titanium dioxide (Degussa P-25) to adsorb U(VI) from water at pH 6 and total inorganic carbonate concentration of 0.01 M. Consequently, the novel material was used to treat DU-contaminated water at a Department of Defense (DOD) site.

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1. Introduction

Titanium dioxide (TiO₂) has strong affinity for uranium adsorption from water [1]. However, the capacity of titanium dioxide to remove uranium from water is greatly reduced by the presence of carbonate ions under neutral to alkaline conditions. The investigation of carbonate ion effects on the removal of uranium from water is important because uranyl carbonate complexes are predominant species in natural water. Moreover, the removal mechanisms of uranium from water in the presence of carbonate is not clearly known. Many researchers have studied the number of carbonate ligands in the adsorbed uranyl species at the titanium dioxide surfaces. The suggested numbers ranged from zero to three. It was observed that when adsorption takes place from sodium uranyl tri-carbonate solution, 1 mol equivalent of carbonate and two of bicarbonate are released into the solution for each mole equivalent of uranyl adsorbed, so that carbonate is not taken up by the adsorbent [2]. A similar mechanism, where protons from surface

hydroxyl groups caused the dissociation of the uranyl carbonate complex was proposed based on the optical spectra and measurement of pH of uranyl solutions containing carbonate ions before and after contact with hydrous titanium oxide [3]. Analogous (CO₃²⁻ retained)/(uranium retained) ratios were also reported by Yamashita et al. [4]. The analysis of carbonate in the titanium dioxide adsorbent showed that the carbonate ions in [UO₂(CO₃)₃]⁴⁻ were released into solution during uranium adsorption.

In contrast to the proposed adsorption of the simple uranyl ion, UO₂²⁺, other researchers have reported the association of uranyl carbonate complexes with surface sites [1,5]. The retention of carbonate was determined with ¹⁴C-labelled sodium tricarbonato-uranate. It was shown that the ratio (CO₃²⁻ retained)/(uranium retained) remained equal to 2.0 regardless of the concentration of uranium, and that the carbonate ion alone was not retained [1]. Ogata et al. [5] found that the ratio of carbonate ion to uranium retained equaled 3.0. The determination of adsorbed uranyl species is further complicated by the adsorption of carbonate onto titanium dioxide [6].

In this study, novel nanocrystalline titanium dioxide was used to treat depleted uranium (DU)-contaminated water. The novel material had greater capacity than Degussa P-25 TiO₂

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to adsorb U(VI). However, inorganic carbonate decreased the capacity of titanium dioxide to remove U(VI) from water. Batch tests, zeta potential measurements, and FTIR spectroscopic studies were used to investigate the effects of inorganic carbonate on U(VI) adsorption by nanocrystalline titanium dioxide. The acquired knowledge was used to treat DU-contaminated water at a Department of Defense (DOD) facility.

2. Material and methods

2.1. Materials

All stock solutions were prepared using Fisher Scientific ACS grade chemicals and deionized water (DI). High purity nitrogen gas (purity 99.999%, AGL Welding Supply Co., Inc., Clifton, NJ) was used in the batch tests. Carbonate stock solution was prepared by adding 7.0 g of sodium bicarbonate (NaHCO_3) to 100 mL DI water. U(VI) solutions were diluted from a 1000 mg/L uranium Spex standard. Degussa P-25 titanium dioxide was obtained from Degussa Corp., OH, US. The nanocrystalline titanium dioxide was produced by hydrolysis of aqueous titanium sulfate solution under controlled conditions. The titanium dioxide powder was continuously washed with DI water until the conductivity of the supernatant was equal to 15 μs . Depleted uranium-contaminated water samples from a Department of Defense site at Aberdeen Proving Ground (APG) were collected at two locations. The first DOD water sample, referred to as Ford Farm (FF), had 2.94×10^{-6} M U(VI), a total alkalinity of 11.2 mg/L as CaCO_3 and pH 7.0. The second DOD water sample, Bomb Throwing Devices (BTD), had a total U(VI) concentration of 2.31×10^{-5} M, total alkalinity of 177 mg/L as CaCO_3 and pH 8.7. The contaminated water was stored in underground storage tanks. The collection method was grab sampling. Total alkalinity was measured using the titrimetric method (SM 2320B), whereas U(VI) concentration was measured using ChemChek Instruments Kinetic Phosphorescence Analyzer (KPA).

2.2. Exchangeable surface sites

An acid–base titration method was used to determine the number of surface sites in accordance with Sigg and Stumm [7]. Enough titanium dioxide powder was added to pure Millipore DI water to make 100 mL of 10 g/L TiO_2 suspension. The pH of the suspension was decreased to pH of 3.0 using HCl, then the mixture was purged for 2 h with N_2 gas to remove dissolved carbonate. After purging, the suspension pH was increased to the point of zero charge (PZC) (pH 5.8), determined by zeta potential measurements, and allowed to equilibrate for 24 h. The suspension was assumed to be in equilibrium, and an excess amount of strong acid (HCl) was added and allowed to saturate the suspension with protons (H^+) for another 24 h. When saturated, the solids in suspension were separated with a 0.2 μm membrane filter, and the supernatant was then back-titrated to pH 5.8 with a strong base (NaOH). The number of surface sites was calculated by subtracting the number of moles of the back-

titrant, NaOH, from the initial number of moles of HCl added, and dividing the result by the weight of the titanium dioxide used.

2.3. Uranium adsorption batch tests

DI water used in the batch tests was placed in beakers covered with acrylic caps. After the water pH was adjusted to 2, it was purged with nitrogen gas for 1 h to remove dissolved carbonate. Aliquots of uranium standard were added to the purged water to make a 1 mg/L uranium solution. A concentration of 1 mg/L was selected for this study to keep U(VI) concentration below the solubility of U(VI) [8,9]. The pH of the uranium solution was adjusted to 5.0 by addition of nitric acid and sodium hydroxide. Sodium chloride, carbonate stock solution, and titanium dioxide stock solution were added to attain 0.01 M NaCl, and the desired total carbonate and TiO_2 concentrations. Batch tests with zero carbonate concentration were purged with nitrogen gas throughout the preparation time. After the pH was adjusted to the desired value, portions of the uniform suspension were transferred into 50 mL centrifuge tubes with no headspace and capped. The centrifuge tubes were placed in a tumbler for 18 h. The temperature imposed for the mixing period was 20 °C. After mixing, the final pH of the solutions in the centrifuge tubes were measured and recorded as the equilibrium pH. The kinetic experimental results showed that the adsorption reached equilibrium in less than 18 h (data not presented). Approximately 1 mL portions of the equilibrium suspensions were centrifuged at $16,250 \times g$ for 10 min. After separation of the solids from the solution, the supernatants were diluted into 10 mL 1% nitric acid solutions. Control blanks without titanium dioxide were incorporated into this study.

2.4. Contaminated water treatment

A filtration unit consisting of three 0.5 ft³ (14.6 L) columns connected in series was assembled in preparation for the treatment of the contaminated water at APG. The columns measured 31 in. (78.74 cm) in height and 6.0 in. (15.24 cm) in inner diameter. Each column was packed with 10 kg of granulated nanocrystalline titanium dioxide with particle size between 16 and 35 US standard mesh (1.19–0.5 mm). The columns were loosely packed. The bulk density of the titanium dioxide was 708.25 kg/m³. One 20 μm sediment inline filter was attached to the filtration assembly ahead of the first titanium column, and another 20 μm sediment filter was added after the last titanium column.

Sampling ports and pressure gauges were attached ahead and across each of the three filtration columns. Titanium dioxide adsorbent in excess of the amount needed to remove U(VI) from the contaminated waters was packed in the columns due to the limited time allowed on site for the treatment of the contaminated water. The water was pumped through the columns in a down-flow mode. The effluent of the filtration system was collected in temporary storage tanks until U(VI) concentration in the treated waters was verified less than the regulatory levels for disposal.

The DU-contaminated water was filtered at a flow volume of 3 L/min. A log of pressure and pH values at set time intervals was kept throughout the filtration process. Samples from all sampling ports were collected and analyzed.

2.5. Zeta potential measurements

The suspension samples used for zeta potential measurements were prepared in a similar way to the batch test samples. Aliquots of the equilibrium suspensions were withdrawn with syringes and injected into a Malvern Instrument Zetasizer 3000 for measurements. Zetasizer 3000 uses Laser Doppler Velocimetry (LDV) to measure the mobility of the charged particles and the mobility is converted to zeta potential by the Henry equation. The conversion of the mobility data to zeta potential was done by Malvern Instruments Zetasizer 3000 supplied software. Reported results were the average of triplicate measurements.

2.6. FTIR spectroscopic measurements

Aliquots of uranium standards were added to 1 L of carbonate-free water in covered beakers to make a 1 mg/L uranium solution. The pH was increased to 5.0 before carbonate stock solutions were added to reach the desired total carbonate to uranium molar ratios. Titanium dioxide was added to make 10 mg/L TiO_2 suspensions. pH values were maintained at 6.0 while the suspensions were mixed with magnetic stirrers for 4 h. Solids were collected using 0.45 μm filters. FTIR spectra of the dry samples were collected using a ThermoNicolet 670 diffractometer equipped with a Centaurus microscope. The spectra were collected in reflection mode at a resolution of 4 cm^{-1} and 200 scans.

3. Results and discussions

3.1. Characterization of the nanocrystalline titanium dioxide

The nanocrystalline titanium dioxide used was identified as 100% anatase by X-ray diffraction using a Rigaku diffractometer equipped with a graphite monochromator. The crystallite size was found to be 6.0 nm using the Sherrer equation. The BET surface area of the adsorbent was measured using N_2 adsorption (Micromeritics ASAP 2010) and found to be 329 m^2/g . The total exchange capacity ($\equiv\text{TiOH}_T$), the maximum number of exchangeable OH groups at the surface, was found to be equal to 5.98 mmol/g. The $\text{p}K_{a1}$ and $\text{p}K_{a2}$ of the acid–base surface reactions of the nanocrystalline titanium dioxide were determined by acidimetric and alkalimetric titration of 10 g/L titanium dioxide in a carbonate free suspension at three different ionic strengths in batch reactors because the equilibration of the surface is a slow process. The titration batch reactions were allowed 24 h to reach equilibrium. The $\text{p}K_{a1}$ and $\text{p}K_{a2}$ were extracted from the titration data by the graphical double extrapolation method [10–12]. $\text{p}K_{a1}$ and $\text{p}K_{a2}$ were 3.8 and 7.8.

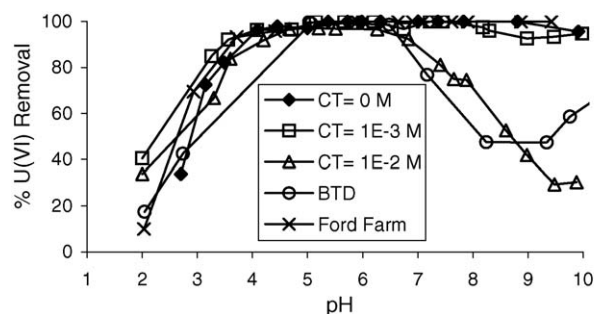


Fig. 1. Plot of the adsorption of 1 mg/L (4.2×10^{-6} M) U(VI) with various total carbonate concentrations (CT), and BT and Ford Farm water on 0.1 g/L titanium dioxide vs. pH.

3.2. U(VI) adsorption edge

U(VI) adsorption edge begins at pH of approximately 2.5. In the absence of carbonate, the removal of U(VI) reached 100% at pH values greater than 3. In the presence of carbonate, the capacity of titanium dioxide to remove U(VI) from water diminished significantly at pH values greater than 6. As example, the efficiency of titanium dioxide to remove U(VI) from water was reduced from 100% at pH of 5 to 70, 40, and 30% at pH values of 7.37, 8, and 9.25, respectively, for total carbonate concentrations of 0.01 M as shown in Fig. 1. BT water with U(VI) concentration of 2.31×10^{-5} M and total carbonate concentration of 1.77×10^{-3} M showed similar adsorption behavior to the synthetic sample with 0.01 M total carbonate content, whereas the Ford Farm sample with total carbonate content of 1.1×10^{-4} M did not exhibit a second adsorption edge at pH values greater than 6.

3.3. Adsorption isotherms

The effect of carbonate on U(VI) removal by titanium dioxide at pH of 6.0 was assessed with the adsorption isotherms in Fig. 2. Approximately 0.02 mol of U(VI) was removed per mole of TiO_2 at equilibrium U(VI) concentration of 0.45 mg/L and with no carbonate in the suspension (CT=0 M). The amount of adsorbed U(VI) decreased substantially with increasing carbonate concentrations. When total carbonate concentration was

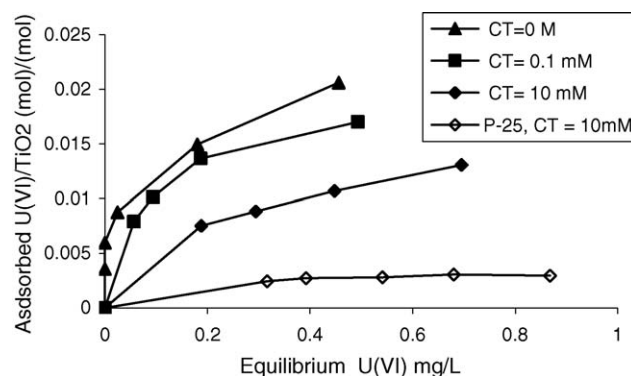


Fig. 2. Carbonate effect on U(VI) adsorption on titanium dioxide in 0.01 M NaCl solution. Initial U(VI) = 1 mg/L (4.20×10^{-6} M); pH 6; temperature = 20 °C.

10.0 mM, U(VI) removal was only 0.01 mol per mole of TiO₂ at U(VI) equilibrium concentration of 0.45 mg/L. It is well known that carbonate adsorbs onto titanium dioxide surfaces [6]. As a result, fewer adsorption surface sites become available to other adsorbates. Aqueous carbonate also forms strong U(VI) complexes such as UO₂CO_{3(aq)}, UO₂(CO₃)₂²⁻, UO₂(CO₃)₃⁴⁻, and (UO₂)₂CO₃(OH)₃⁻ [9,13], which might have lower affinity for surface sites. Carbonate might compete with U(VI) for adsorption sites and it also competes with surface sites to complex U(VI).

It is interesting to note that the capacity of nanocrystalline dioxide is approximately four times the capacity of Degusaa P-25 to adsorb U(VI) from water at pH 6, total inorganic carbonate concentration of 10 mM, and equilibrium U(VI) concentration of 0.4 mg/L (Fig. 2). Approximately 0.0025 mol of U(VI) was removed per 1 mol of P-25 titanium dioxide, whereas the removal was approximately 0.01 mol of U(VI) per 1 mol of nanocrystalline titanium dioxide.

3.4. Zeta potential measurements

The zeta potential of the titanium dioxide surfaces covered with U(VI) and carbonate can provide valuable information on the surface forms of the adsorbates because the formation of the surface complexes will change the surface charge. The results in Fig. 3 showed that the titanium dioxide had a positive surface charge up to approximately pH of 5.8, the point of zero charge. At higher pH values, the surface charge became negative. After U(VI) was loaded onto the titanium dioxide surface in the absence of carbonate, the PZC shifted from approximately 5.8 to 6.2. The increased zeta potential suggested that U(VI) was adsorbed in cationic forms. In the absence of carbonate, the major U(VI) species present at a neutral pH range are UO₂²⁺, UO₂OH⁺, (UO₂)₅(OH)₅⁺, and (UO₂)₄(OH)₇⁺ [13,14]. The adsorption of uranium on the titanium dioxide surfaces in the absence of carbonate resulted in an increase of the surface charge at pH 6.0. The adsorption of all possible U(VI) hydroxide complexes will result in the formation of anionic or neutral surface species, which contradicts the increased zeta potential caused by U(VI) adsorption [13]. The only possible cationic surface species is monodentate uranyl, ≡S–O–UO₂⁺, where ≡S–O

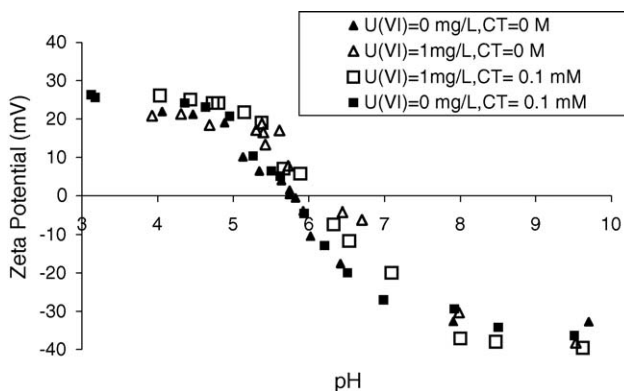


Fig. 3. Effect of U(VI) and total carbonate (CT) adsorption on zeta potential of titanium dioxide surface. TiO₂ = 10 mg/L; NaCl = 0.01 M.

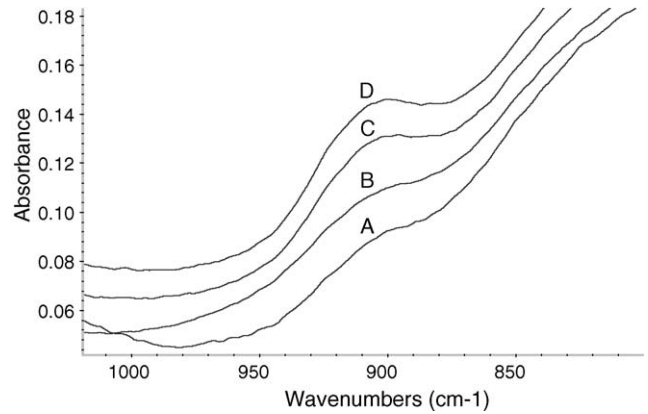
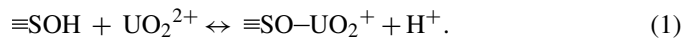


Fig. 4. FTIR spectra of U(VI) adsorbed on titanium dioxide surface at pH 6 and TiO₂ = 10 mg/L: (A) total carbonate (CT) = 1 × 10⁻⁴ M and U(VI) = 0 M; (B) CT = 0 M and U(VI) = 0 M; (C) CT = 0 M and U(VI) = 4.2 × 10⁻⁶ M; (D) CT = 1 × 10⁻⁴ M and U(VI) = 4.2 × 10⁻⁶ M.

denotes a titanium dioxide surface site. Based on the zeta potential results, the U(VI) adsorption is written as:



In the presence of U(VI) and carbonate, there was an increase in the surface charge at pH > 5.0. Monodentate adsorption of uranyl ion alone, or monodentate adsorption of uranyl ion in addition to adsorption of uranyl carbonate complexes, might explain the increase in surface charge. The FTIR spectra of the titanium dioxide in the presence of U(VI) and carbonate will help further delineate the nature of the U(VI) species at the titanium dioxide surface.

3.5. FTIR spectroscopic studies

The antisymmetric stretching vibration of the adsorbed uranyl ion UO₂²⁺ on the titanium dioxide surface was investigated in the presence and absence of carbonate. The coordination of carbonate ligands with the uranyl ion will cause a decrease in the energy number of the antisymmetric stretching vibration of UO₂²⁺ [13,15–20].

Titanium dioxide had a small shoulder in the 900 cm⁻¹ region as shown in Fig. 4, and as reported by Castellano et al. [21]. Upon loading the surface with U(VI) in the absence of carbonate, a UO₂²⁺ strong antisymmetric stretching vibration shoulder appeared in the 900 cm⁻¹ region. When both carbonate and uranium were introduced to the system, the antisymmetric stretching vibration of UO₂²⁺ shoulder did not shift toward smaller wavenumbers as was the case of uranium and carbonate adsorption on hematite [22] and ferrihydrite [13]. The ionic strength and the pH values were held constant during the FTIR experiments. The lack of shift of the UO₂²⁺ stretching vibration, or lack of the broadening of the antisymmetric stretching vibration of UO₂²⁺ shoulder toward the lower energy side as carbonate concentration increased, indicated that uranium was adsorbed as a uranyl ion, UO₂²⁺. Based on the FTIR and zeta potential results, the adsorption of U(VI) onto the titanium dioxide surface

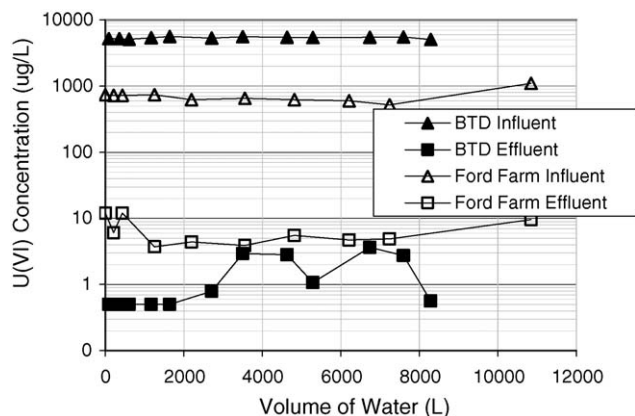


Fig. 5. U(VI) concentration in the influent and effluent of the filtration unit vs. the volume of the treated water.

in the presence and absence of carbonate is written as:



Even though carbonate has an out-of-plane ν_2 C–O bending vibration that exhibits in a region between 880 and 835 cm^{-1} [23,24], no clear peak or shoulder could be assigned to this vibration when titanium dioxide was treated with 1×10^{-4} M of total carbonate solution (spectrum A in Fig. 4). The FTIR spectra of blank (only titanium dioxide) and carbonate-treated titanium dioxide samples were similar. The absence of carbonate peaks or shoulders could be attributed to the low intensity of the ν_2 C–O bending vibration of the adsorbed carbonate.

3.6. Contaminated water treatment

The treatment results of the BTD and Ford Farm DU-contaminated water at APG are shown in Fig. 5. The concentration of U(VI) in the influent and effluent were plotted versus the volume of treated water. The initial U(VI) concentrations were approximately 5200 and 700 $\mu\text{g/L}$ for the BTD and Ford Farm waters, respectively. The concentration of U(VI) in the effluent was less than approximately 10 $\mu\text{g/L}$.

4. Conclusions

Nanocrystalline titanium dioxide was successfully used to treat DU-contaminated waters with total alkalinity of 177 mg/L as CaCO_3 and pH 8.7. The nanocrystalline titanium dioxide had four times the capacity of Degussa P-25 titanium dioxide to remove U(VI) from water at pH 6 and CT of 0.01 M. The reduced capacity of titanium dioxide to adsorb U(VI) in the presence of carbonate was attributed to the shifting of the chemical equilibrium in favor of aqueous uranyl–carbonate complexes as carbonate concentration was increased. As total carbonate concentration increases, aqueous multi-carbonate U(VI) complexes become more predominant and start forming at lower pH [13]. Even though carbonate adsorption on the titanium dioxide surface could reduce the number of the sites available for uranium adsorption, it is postulated that the aqueous carbon-

ate complexation of uranium was the predominant mechanism responsible for the hindrance of the uranium uptake. More U(VI) was removed by titanium dioxide in the presence of carbonate at pH 5.0 than at pH > 8.0; U(VI) removal was 100% at pH 5, whereas it was only 70% at pH 8 for CT of 0.01 M (Fig. 1). However, the number of surface sites occupied by total carbonate at pH 5.0 is greater than the number of surface sites occupied by total carbonate at pH 8.0 because total carbonate adsorption on the titanium dioxide surface is higher at pH 5.0 than at 8.0 [14]. Therefore, the reduced uranium removal in the presence of carbonate was not the result of the competition of carbonate with uranium for adsorption sites, but rather the competition of aqueous carbonate with surface sites to complex uranium.

Acknowledgements

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