Dissolution of uranium metal without hydride formation or hydrogen gas generation

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ABSTRACT

This study shows that metallic uranium will cleanly dissolve in carbonate-peroxide solution without generation of hydrogen gas or uranium hydride. Metallic uranium shot, 0.5–1 mm diameter, was reacted with ammonium carbonate–hydrogen peroxide solutions ranging in concentration from 0.13 M to 1.0 M carbonate and 0.50 M to 2.0 M peroxide. The dissolution rate was calculated from the reduction in bead mass, and independently by uranium analysis of the solution. The calculated dissolution rate ranged from about 4×10^{-3} to 8×10^{-3} mm/h, dependent primarily on the peroxide concentration. Hydrogen analysis of the etched beads showed that no detectable hydrogen was introduced into the uranium metal by the etching process.

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1. Introduction

Uranium is a reactive metal and corrodes in water, forming hydrogen gas, uranium hydride, and uranium compounds in various oxidation states [1–4]. After uranium metal has been left in contact with water (either liquid or vapor) in the presence of atmospheric oxygen for a period of months or years, the result is badly corroded uranium covered with sludge of indefinite composition. The composition of the corrosion product depends partly on the mechanical configuration – uranium hydride tends to form in protected areas such as crevices, and uranyl ion accumulates on the surface where it may recrystallize into yellow salts [5,6]. The mixture may be pyrophoric from uranium hydride [7]. As the metal disintegrates, fine metallic particles may form and increase the pyrophoricity hazard. Hydrogen gas formed by direct reaction of uranium metal with water and by hydrolysis of uranium hydride may create a flammability hazard.

One example of corroded uranium metal is at the US Department of Energy Hanford site K Basins, where irradiated metallic uranium fuel was stored under water for many years. Some of the fuel cladding failed, allowing the metallic fuel inside to corrode badly. The corrosion adds pyrophoricity and flammability hazards to fuel, which already had hazards of fission products, high gamma dose rates, and transuranic elements.

This study is an investigation of a method to dissolve the uranium metal without forming hydrogen gas or uranium hydride, and without risking a runaway reaction with uranium, which is a reactive metal. Uranium metal will dissolve vigorously in any of

several strong acid mixtures, but these reactions generate a large volume of gases and much heat. If kilogram quantities of uranium metal were dissolved in, say, 12 M nitric acid, the result would be a spectacular and distinctly unsafe reaction.

Uranium metal will dissolve readily in many solvents, almost always accompanied by the generation of hydrogen gas. Many different means have been devised to dissolve uranium metal for analysis [8–11]. The dissolution means devised for analysis of uranium metal are not intended to avoid hydrogen generation; they are only intended to safely dissolve a small quantity of the metal and produce a solution suitable for further chemistry. The amount of metal dissolved for analysis is usually very small, typically a gram or less. A method suitable for an analytical scale cannot be assumed safe and appropriate for dissolving kilograms of corroded uranium.

Uranium forms a series of strong, stable carbonate complexes which cause uranium compounds and uranium metal to dissolve more or less readily in carbonate solution under oxidizing conditions. The oxides UO_2 and U_3O_8 dissolve readily in carbonate solutions under moderately oxidizing conditions. Uranium ores are frequently leached with sodium carbonate solution to dissolve the uranium [12]. Uranium metal also dissolves in dilute carbonate solution under moderately oxidizing conditions. The only real questions are the rate, which could be too slow for some applications, and the possibility of formation of hydrogen gas and uranium hydride.

This study measured the rate that uranium metal shot dissolves in dilute ammonium carbonate + hydrogen peroxide solutions of varying concentrations under conditions of moderate stirring. Ammonium carbonate was chosen because it is volatile; it can be evaporated readily from boiling water and distilled as a solid.

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Hydrogen peroxide was chosen as the oxidizing agent because it can be easily decomposed to water and oxygen. (Hydrogen peroxide is also a strong ligand for uranyl ion, similar to carbonate.) Thus, the process can dissolve uranium metal without adding any bulk beyond the volume of the uranium compounds formed.

Additionally, ammonium carbonate and hydrogen peroxide are not very corrosive, either together or separately. This mixture could be used in standard stainless steel equipment without directly causing any corrosion.

2. Measurement of dissolution rate of U metal

2.1. Gravimetric measurement of dissolution rate

Saturated ammonium carbonate solution was made by shaking solid ammonium carbonate (Fisher HPLC grade) with deionized water at room temperature (21 °C). The ammonium carbonate used is actually a mixture of ammonium carbonate and ammonium carbamate. The pH of this solution was about 10.

The absolute carbonate concentration of the saturated solution was measured (in duplicate) gravimetrically by calcium carbonate precipitation. The measured carbonate concentration was 1.32 and 1.30 M.

Hydrogen peroxide (30%) was used as a peroxide stock solution. To measure the actual peroxide concentration, the stock hydrogen peroxide was diluted tenfold with 0.1 M nitric acid and then titrated against 0.101 M potassium permanganate solution. The peroxide assay was done in duplicate. The assay results were both 10.2 M.

The uranium shot consisted of 0.5–1.0 mm diameter spheres (from stock on hand at Pacific Northwest National Laboratory), and appeared dark and metallic, free of loose corrosion and dust. To measure the distribution, 369 beads were individually weighed. The beads ranged from 0.0012 to 0.0110 g, with an average of 0.0041 ± 0.0018 g. Using a density of 19.05 g/cm^3, the calculated diameter ranged from 0.49 to 1.03 mm. The surface area ranged from 0.77 to 3.3 mm^2.

Six tests were set up with the starting conditions shown in Table 1. Each test was designed to use approximately 0.05 g of uranium shot. This quantity of uranium shot would not materially change the concentrations of the reactants, even if most of the uranium dissolved. Thus, the experimental conditions would remain constant throughout the test.

Test solutions were made by mixing appropriate volumes of 1.31 M $(NH_4)_2CO_3$ solution, 10.2 M H_2O_2, and water. The test solutions were made immediately before they were used, so that the concentrations would not be changed by evaporation of ammonium carbonate and decomposition of hydrogen peroxide. All the solutions were at room temperature (21 °C).

First, the solutions were mixed in labeled 150-mL glass beakers. Then the uranium shot for each test was weighed in an aluminum weigh boat and the number of beads was counted. Finally, the uranium shot was added to the solution and the starting time was recorded for each sample. The solution was then stirred for approximately 1 h.

All six solutions began to turn yellow within several minutes of stirring. None of the tests showed any evidence of gas evolution. The uranium shot rolled freely around the beakers as the solutions were stirred.

After stirring for about an hour, the solution was sluiced into another container, and the ending time was recorded. The reacted uranium metal shot was washed twice with several mL of deionized water, then twice with several mL of dry ethanol. The beads were air dried, then dried for several minutes under a heat lamp. After drying, the reacted uranium beads were weighed. The dry, reacted uranium beads were clean and silvery, with no visible corrosion or tarnish.

2.2. Results of gravimetric dissolution rate tests

The test conditions for the initial dissolution rate tests are given in Tables 1 and 2. The amount of uranium that dissolved in each test is too small to consume a significant fraction of the reactants. Each mole of uranium metal requires three moles of peroxide for oxidation. Each mole of uranyl formed uses as many as three moles of carbonate (when excess carbonate is present, as is the case in these tests).

The dissolution rates were calculated from the reduction in average uranium bead diameter, and are shown in Table 3. Because the beads vary in diameter, the calculated dissolution rates have several percent uncertainty from the uncertainty in surface area.

The measured dissolution rate depends significantly on the peroxide concentration and to a smaller extent on the carbonate concentration. These dissolution rates are for a mechanically stirred solution, agitated enough to avoid localized depletion of reactants around the dissolving uranium. The reacting uranium does not generate any significant convection on its own. If the reaction mixture were not stirred during the uranium dissolution, then the rate would surely decrease, since the metal dissolves fast enough to reduce the local concentration of reactants.

The exposed surface area of the beads did not change much during the tests, since the diameter of the beads changed only a little.

2.3. Measurement of dissolution rate by kinetic phosphorescence

A second, more accurate test was conducted to confirm these dissolution rates. This test was done in the same manner, except that the pieces of uranium shot in each test were closely matched in weight (to make the diameters more uniform) and the dissolved uranium concentration was measured at intervals by kinetic phosphorescence, which can measure the dissolved uranium much more accurately than measuring mass to ±0.1 mg. We used a model KPA-11R uranium analyzer made by Chem-Chek Instruments, Richland, WA. The analytical range of this instrument is from about 2×10^{-5} to 0.5 ppm uranium in solution. The precision is about ±3% at one standard deviation.

Table 1
Gravimetric dissolution rate test conditions

Test	Total solution volume (mL)	CO_3^{2-} Conc. (M)	H_2O_2 Conc. (M)	Number of U beads	Starting mass of U (g)	Elapsed time (min)	Ending mass of U (g)
#1	89	1.01	0.50	10	0.0514	55	0.0505
#2	89	1.01	1.01	14	0.0529	58	0.0512
#3	89	1.01	2.02	17	0.0572	61	0.0544
#4	72	0.51	1.01	18	0.0526	45	0.0509
#5	72	0.25	1.02	16	0.0508	48	0.0493
#6	72	0.13	1.01	13	0.0541	50	0.0529

Table 2
Changes in test conditions during gravimetric test

Run	Moles U dissolved	Moles CO_3^{2-} consumed	Moles H_2O_2 consumed	Product uranium molarity
#1	3.78E−6	1.13E−5	1.13E−5	4.24E−5
#2	7.14E−6	2.14E−5	2.14E−5	8.04E−5
#3	1.18E−5	3.53E−5	3.53E−5	1.32E−4
#4	7.14E−6	2.14E−5	2.14E−5	9.87E−5
#5	6.30E−6	1.89E−5	1.89E−5	8.74E−5
#6	5.04E−6	1.51E−5	1.51E−5	6.96E−5

Table 3
Change in diameter, surface area, and mass

Test	Estimated diameter and surface area				Mass lost (g)	Elapsed time (h:min)	Dissolution rate (mm/h)
	Average starting diameter per bead (mm)	Total starting surface area (mm^2)	Average ending diameter per bead (mm)	Total ending surface area (mm^2)			
#1	0.802	20.2	0.797	20.0	0.0009	0:55	0.0026
#2	0.724	23.0	0.716	22.5	0.0017	0:58	0.0041
#3	0.696	25.9	0.685	25.0	0.0028	1:01	0.0057
#4	0.664	24.9	0.657	24.4	0.0017	0:45	0.0048
#5	0.683	23.4	0.676	23.0	0.0015	0:48	0.0042
#6	0.747	22.8	0.742	22.5	0.0012	0:50	0.0033

If the uranium shot used in these tests started out with a significant amount of corrosion, then the measured dissolution rates would be biased high by the amount of readily-soluble corrosion on the metal. To avoid this error, the uranium shot used in this test was first cleaned with a dilute ammonium carbonate, hydrogen peroxide solution, then rinsed with deionized water, then rinsed with ethanol and dried. The clean, dry uranium shot was silver colored and appeared completely free of corrosion and black surface film.

The carbonate concentration was kept constant at 1.0 M, and the peroxide concentration was varied. The test was conducted at room temperature. Samples were drawn after 1, 10, 20, 30, 40, and 60 min and analyzed for uranium by kinetic phosphorescence. The test conditions and calculated reduction in beak diameter are given in Table 4.

2.4. Results of kinetic phosphorescence measurement

The measured uranium concentration increased linearly with time, as shown in Fig. 1. The solid lines are linear regression fits

to each set of data. The linearity of the data and the intercept of zero show that uranium shot did not have significant surface corrosion at the beginning of the test. The dissolution rate is proportional to the exposed uranium surface area (assuming constant stirring, reactant concentrations, and temperature). Because the surface area did not change much during the test, the dissolution rate is nearly constant.

The calculated dissolution rates, shown in Table 4, are approximately equal to the previously measured dissolution rates.
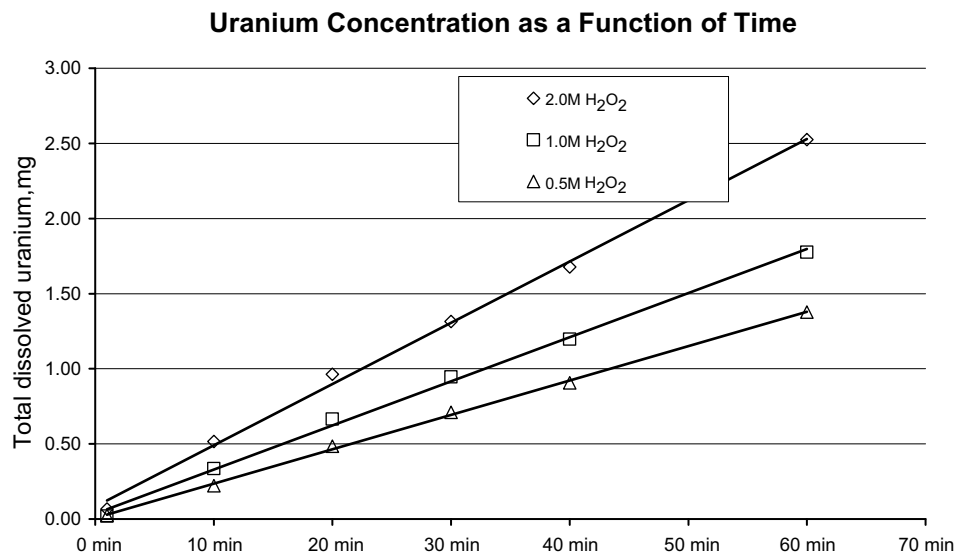
3. Measurement of hydrogen generation

A separate series of tests were conducted to measure any hydrogen that might be formed and dissolved into the sample as the uranium metal dissolves in the carbonate-peroxide solution. The uranium metal was reacted as before, then analyzed for total hydrogen content. As a comparison, uranium metal was also reacted with 2 M HCl, a reaction which liberally generates hydrogen. To distinguish hydrogen generated during the etching process from

Table 4
Calculated dissolution rate, measured by kinetic phosphorescence

Test #	Molarity of H$_2$O$_2$	Average starting bead wt (mg)	Average ending bead wt (mg)	Average starting radius (mm)	Average ending radius (mm)	Dissolution rate (mm/h)
#1a	0.5	3.493	3.401	0.427	0.423	0.0038
#2a	1.0	3.413	3.295	0.424	0.419	0.0050
#3a	2.0	4.283	4.073	0.457	0.450	0.0076

Fig. 1. Uranium concentration as a function of time, measured by kinetic phosphorescence.

hydrogen that might have already been in the uranium metal, the carbonate-peroxide solutions were prepared in D_2O instead of H_2O.

The hydrogen generation tests ran for 10 min and 100 min. Uranium beads between 3 and 4 mg were used. The 10-min tests used single beads that were not accurately weighed, since the weight loss in only 10 min was expected to be too small to measure by weighing. The 100-min tests used more beads and were accurately weighed before and after exposure to the etch solutions. Two unexposed uranium beads were used as blanks. The test conditions are given in Table 5.

3.1. Results of hydrogen generation tests

Hydrogen gas release was measured as a function of temperature using a custom gas mass spectrometer system fabricated at PNNL [13]. The analysis procedure involved dropping individual specimens, under vacuum, into a small cylindrical ceramic crucible whose temperature was increased in a very nearly linear profile from ~40 °C to ~1200 °C at a rate of ~100 °C/min. Prior to analysis, the crucible was pre-heated to ~1300 K under high vacuum for several days to reduce hydrogen background. Before initial vacuum pumping, the sample chamber and crucible volume were subjected to a low-pressure (~200 mTorr) argon discharge for ~30 min to aid in the desorption of water that could be dissociated by the hot crucible during analysis and thus contribute to the measured hydrogen release. During the pre-heating

and subsequent analysis, the sample chamber was maintained at room temperature.

Hydrogen release was measured using a Stanford Research Systems Model RGA-100 quadrupole mass spectrometer connected to the crucible volume. The RGA-100 was interfaced to a standard computer (PC) which provided both system control and data output. Primary calibration of the system sensitivity was accomplished using a Vacuum Technology Inc. hydrogen leak source of 1.03×10^{-10} mol H_2/s, with a stated NIST-traceable absolute uncertainty of ±15% (3σ). Calibration measurements were conducted following each set of analysis runs. Secondary calibration for HD and D_2 was based on the relative atomic mass (M) of each species using the function $(1/M)^{1.25}$.

The results of the hydrogen release measurements are shown in Figs. 2–4 for the un-reacted uranium, the carbonate reacted uranium, and the HCl reacted uranium, respectively. Each plot shows the various hydrogen species release rate on the left axis versus the heating time. The temperature profile is shown in the right axis, also as a function of time.

The hydrogen generation tests showed no measurable hydrogen release when uranium metal was dissolved in a carbonate-peroxide solution. The D_2 and HD release from the reacted specimens were no different than that from the unexposed controls. In each case, the total integrated deuterium release was $<1 \times 10^{12}$ atoms, which was at the background level for the mass spectrometer system. The sample reacted for 10 min in 2 M HCl, in contrast, showed

Table 5
Test conditions for hydrogen generation tests

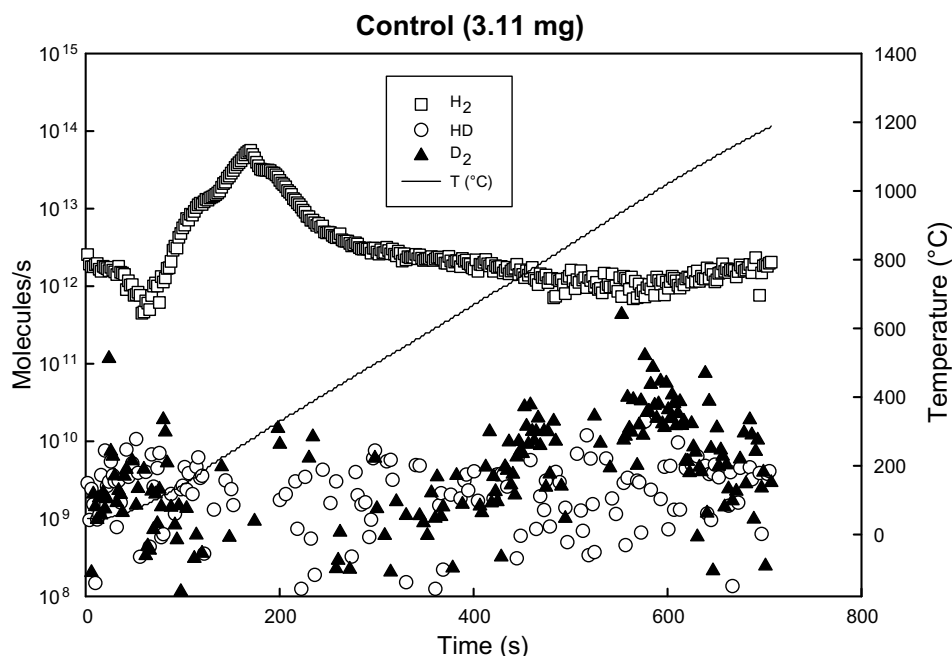| Sample	Dissolution solution	Number of U beads	Starting mass of U metal (mg)	Duration of etch (min)	Ending mass of U metal (mg)
#2	$(NH_4)_2CO_3 + H_2O_2$	1	3–4	10	Not weighed
#3	$(NH_4)_2CO_3 + H_2O_2$	22	77.0	100	68.8
#5	2 M HCl	1	3–4	10	Not weighed
#6	2 M HCl	24	107.6	100	Completely dissolved
Blank 1	None	1	3–4	None	
Blank 2	None	1	3–4	None	

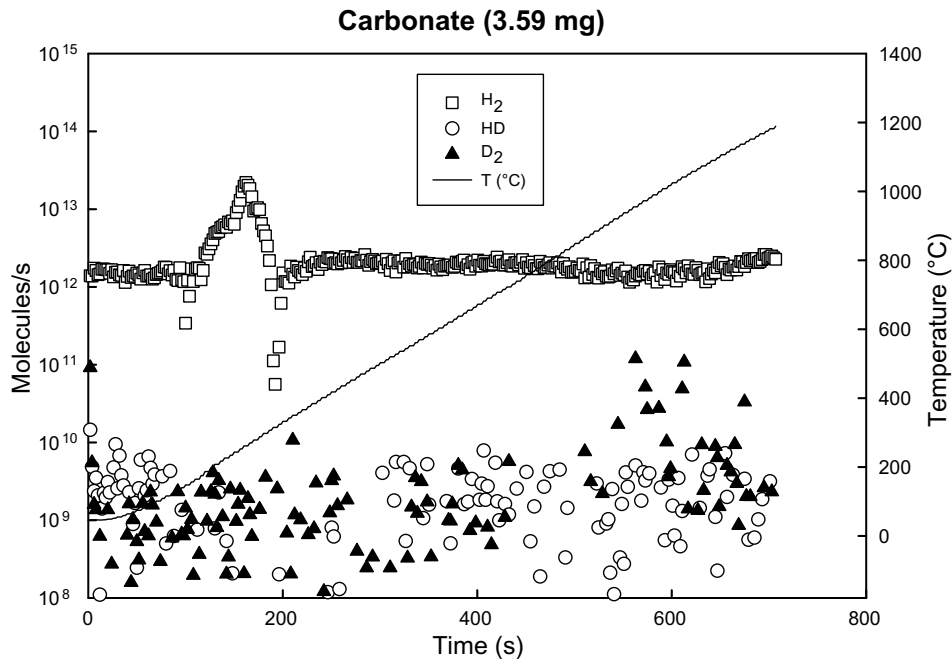**Fig. 2.** Hydrogen release from un-etched (control) uranium metal.

Fig. 3. Hydrogen release from carbonate leached uranium metal.

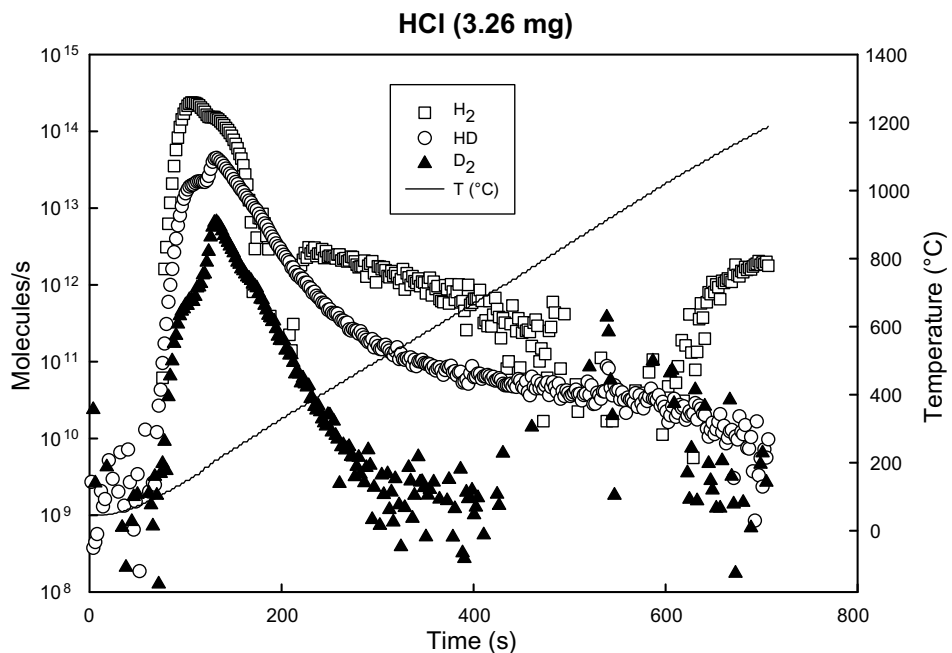**Fig. 4.** Hydrogen release from HCl leached uranium metal.

an integrated deuterium release of ~2.5 × 10^{15} atoms, or about 300 appm relative to the uranium. (The sample reacted for 100 min in 2 M HCl completely dissolved.)

4. Discussion

Hydrogen, as H$_2$, is apparently not involved in the reaction between uranium metal and a carbonate–peroxide solution. The oxidation of uranium metal by peroxide in carbonate solution must overwhelm the oxidation of uranium metal by water, since no hydrogen is generated. The overall oxidation of uranium metal in carbonate-peroxide solution apparently follows the stoichiometry in Eq. (1), which does not involve reduction of water or hydrogen ion by uranium metal:

$$U + 3H_2O_2 + 3CO_3^{2-} \rightarrow UO_2(CO_3)_3^{4-} + 2OH^- + 2H_2O \tag{1}$$
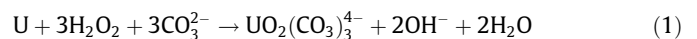
The final uranyl specie may not be purely the tricarbonate; other species are possible. Peroxide is also a good ligand for uranyl and can substitute for carbonate, depending on the carbonate and peroxide concentrations. We did not identify the actual uranyl species present in the solutions produced by carbonate-peroxide etching.

From this stoichiometry, it is possible to infer a few clues about the reaction mechanism. Carbonate is well known to be an excellent complexing agent for uranyl ion, and is also known to be a good complexing agent for uranium(IV). Carbonate may also be a good complexing agent for uranium(III), if uranium(III) behaves like the trivalent lanthanides, which are known to form carbonate complexes. (Walter [14] was able to load scandium onto an anion exchanger in carbonate solution, but the results were erratic. In unpublished work in this author's laboratory, neodymium could be loaded onto an anion exchanger from 0.05 M ammonium carbonate solution, but the results were erratic, probably because of low solubility of the neodymium carbonate.) Carbonate may ligate the uranium as the uranium is oxidized through several oxidation states.

Peroxide is also a good ligand for uranyl ion. It may also be a good ligand for uranium(IV), but it quickly oxidizes U(IV) to UO_2^{2+}. Between the peroxide and the carbonate, the uranium may have many stable complexes that it can smoothly pass through as it is oxidized, finally arriving in the very stable complex $UO_2(CO_3)_3^{4-}$ or a mixed carbonate-peroxide complex.

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