

Kinetic Study of the Oxidative Dissolution of UO_2 in Aqueous Carbonate Media

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The oxidative dissolution of uranium(IV) dioxide powder at room temperature in aqueous carbonate media has been investigated. Kinetic studies evaluating the efficacy of various oxidants, including $\text{K}_2\text{S}_2\text{O}_8$, NaOCl , and H_2O_2 , for dissolving UO_2 in alkaline solution have been performed, with H_2O_2 exhibiting the most rapid initial dissolution at 0.1 M oxidant concentrations. This result is due in part to the ability of peroxide to act as both an oxidant and a ligand under alkaline conditions. A spectrophotometric titration was used to confirm peroxide coordination to the U(VI) metal center. The disappearance of characteristic absorbance maxima associated with $\text{UO}_2(\text{CO}_3)_3^{4-}$ (e.g., 448.5 nm) and a subsequent change in solution coloration upon titration with hydrogen peroxide indicated a change in speciation. Optimization of the hydrogen peroxide concentration indicated that the initial rate of uranium oxidation increased with increasing peroxide concentration, with a maximum reaction rate estimated at about 0.9 M peroxide. In addition, the effects of both the carbonate counteraction and the carbonate concentration were also studied. It was determined that for 40 mg UO_2 0.5 M Na_2CO_3 was the most propitious choice, exhibiting both a high initial dissolution rate and the highest UO_2 dissolution capacity among the systems studied.

Introduction

Understanding the dissolution of UO_2 is critical for improving nuclear fuel reprocessing methods and for modeling the corrosion behavior of spent nuclear fuel (SNF) under repository conditions.^{1–4} To date, the PUREX liquid–liquid extraction process is the only technology that has been employed at a significant scale to reprocess spent nuclear fuel, despite shortcomings such as the use of flammable organic solvents, the occurrence of radiation-induced solvent degradation,^{5,6} and the loss of minor actinides among fission product waste.⁷ In order for nuclear power to be a viable energy source in the future, reducing the volume and disposal costs of high-level radioactive material is essential. This requires the development of new SNF reprocessing approaches that enable the separation of fission products from actinides in a more environmentally friendly and less costly manner.

Historically, SNF reprocessing has been done using acidic media, such as nitric, sulfuric,⁸ and phosphoric acids,⁹ with nitric acid being most commonly used. Some researchers have reported using mineral acids in conjunction with synergistic agents, including O_2 ,¹⁰ O_3 ,¹¹ ultraviolet light,¹² and noble metal catalysts,¹³ to enhance the rate of uranium oxidation. Moreover, non-aqueous approaches have also been described for dissolving UO_2 , including the use of supercritical CO_2 ^{14–16} and high-temperature molten salts.^{17,18}

An obvious alternative to acidic UO_2 dissolution is the use of alkaline solutions. For many years, hydroxide has been used in the presence of an oxidant, such as NaOCl

or H_2O_2 , to dissolve uranium metal and its alloys.^{19–21} These two oxidants are especially applicable for studying UO_2 dissolution as it pertains to long-term geological disposal because they are the radiolysis products of brine²² and water,²³ respectively. Several studies have been reported using NaOCl ²³ and H_2O_2 ^{24,25} in alkaline media to determine both corrosion of the UO_2 surface^{26,27} and dissolution kinetics.²⁵ In addition to hydroxide systems, UO_2 dissolution behavior in carbonate systems has also been studied. Oxidizing carbonate solutions are often studied, because they can aid in predicting the environmental fate of UO_2 in natural groundwaters.^{1,2,27} Furthermore, carbonate solutions exhibit a high capacity for dissolved uranium, based on the formation of a highly soluble anionic solution complex, $\text{UO}_2(\text{CO}_3)_3^{4-}$.²⁸ Because uranyl triscarbonate is the predominating species, many researchers have evaluated aqueous bicarbonate–carbonate solutions as a possible medium for UO_2 dissolution.^{29–33} Several oxidants have been used in such instances, including O_2 ,^{31,32,34} NaOCl ,³⁰ MnO_4^- ,³⁵ MnO_4^{2-} ,³⁵ and H_2O_2 .³⁶ Uranium oxidation has also been accomplished by applying an anodic potential.^{33,37} In addition, electrochemical studies of UO_2 corrosion in aqueous carbonate media have also been reported.^{38, 39}

In the work presented herein, the efficacy of various oxidants, including NaOCl , $\text{K}_2\text{S}_2\text{O}_8$, and H_2O_2 , for dissolving UO_2 in aqueous carbonate solutions was evaluated. With hydrogen peroxide as the oxidant, the effects of both the carbonate counteraction and the carbonate concentration on the initial dissolution rate and dissolution capacity were studied and optimized. To better understand the chemistry that is occurring (for process development), speciation of the dissolution products was also studied.

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Experimental Section

Reagents. Lithium, sodium, potassium, cesium, and ammonium carbonate salts; potassium peroxydisulfate; hydrogen peroxide; and sodium hypochlorite were all ACS grade and used as received. All solutions were prepared from distilled deionized water with a specific resistance of 18.2 M Ω ·cm. The concentration of hydrogen peroxide was determined from the manufacturer's lot number, whereas the concentration of sodium hypochlorite (3.5 M) was determined spectrophotometrically at 290 nm with $\epsilon = 350 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$.²² The medium-fired (500–700 °C) uranium dioxide powder used in all experiments was produced at Los Alamos National Laboratory. The BET surface area of the UO₂ was determined to be 1.17 m²·g⁻¹. The particle size distribution of the uranium dioxide was determined by a Coulter counter in ISOTON II buffer solution and was found to be bimodal in nature with mean particle diameters of 8.7 and 15.1 μm .

Dissolution Studies. As a general procedure, aqueous carbonate solution was added to 170 mmol of UO₂ (equivalent to 70 mM if dissolved), followed by the subsequent addition of peroxide to result in a 0.7 M H₂O₂ solution for most experiments. (Note: The order in which reactants are added dramatically affects the UO₂ dissolution rate, with the aforementioned sequence yielding the most rapid kinetics.) For peroxide optimization experiments, 0.5 M Na₂CO₃ was added to 170 mmol of UO₂, followed by the subsequent addition of varying concentrations of H₂O₂. In contrast to the general dissolution procedure described above, deviations were made when determining the most efficacious oxidant. In this case, initial reactant concentrations were 74 mM UO₂ (if dissolved), 1 M K₂CO₃, and 0.1 M oxidant. For elapsed reaction time determinations, dissolution was initiated by the addition of H₂O₂ and terminated by filtering the reaction mixture through a 0.2- μm nylon or Teflon syringe filter. CAUTION: This reaction is extremely exothermic and effervescent. Caution should be exercised when adding hydrogen peroxide to a UO₂/carbonate mixture.

Determination of Molar Extinction Coefficients for Uranium Determination. A Varian Cary 500 or 600 UV–vis–NIR spectrophotometer was used to collect absorbance spectra. The concentration of U(VI) in solution following dissolution was determined by acidifying aliquots of filtered solutions with 2 M HCl. Dissolution vials were allowed to sit until effervescence ceased (typically 4 h) prior to dilution/acidification. The apparent molar extinction coefficient of uranyl(VI) at 413 nm was determined as a function of chloride concentration. This was done using a regression equation (ϵ vs [Cl⁻]) that was obtained from the molar extinction coefficients of uranyl(VI) in 0.1, 1, 3, and 5 M NaCl solutions. The spectroscopic characterization of uranyl(VI) in chloride media is the topic of a future publication. The molar extinction coefficient of UO₂(CO₃)₃⁴⁻ was determined spectrophotometrically. The mean molar extinction coefficient, obtained from greater than 30 samples, was found to be 26.2 \pm 0.8 at 448 nm.

In some instances, uranium concentration was determined using the molar extinction coefficient of a red solution species formed during dissolution ($\epsilon = 142 \pm 1$ at 500 nm). Individual dissolution reactions containing 0–70 mM uranium, 0.5 M Na₂CO₃, and 0.7 M H₂O₂ were performed. Reactions were run for at least 30 min

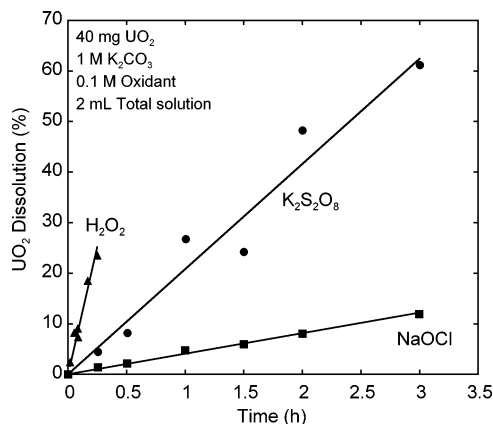
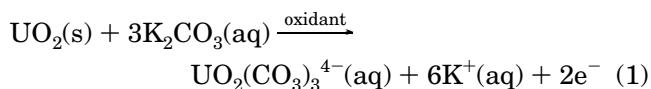


Figure 1. Comparison of various oxidants for dissolving UO₂ powder in aqueous carbonate media. Solid lines indicate the region over which the initial dissolution rates were calculated.

to ensure complete UO₂ dissolution. Aliquots of the resultant red solution were diluted in 0.5 M Na₂CO₃ prior to UV–vis measurements in order to adhere to the Beer–Lambert law. Absorbance values were taken at 500 nm for consistency because the decomposition of peroxide in alkaline solutions and subsequent alteration of the solution species distribution causes spectral changes below 475 nm. The two methods used for determining uranium concentration (direct measurement and acidification) were in agreement to within $\pm 5\%$.

Results and Discussion

Initial studies were performed to determine the propensity of UO₂ to dissolve in pure carbonate aqueous media. It was observed that, in the absence of an oxidizing agent, the chemical dissolution of UO₂ does not significantly occur within several hours; this is in stark contrast to its dissolution behavior in acidic solutions. On the basis of this result, several common oxidizing agents, including ozone, potassium peroxydisulfate, hydrogen peroxide, and sodium hypochlorite, were evaluated for their ability to oxidize U(IV) to U(VI) and facilitate dissolution of the oxide. A carbonate solution saturated with ozone was unable to dissolve the UO₂ to any measurable extent, and therefore, ozone was not studied further. For all other oxidants, a concentration of 0.1 M was used for comparison because of the limited solubility of K₂S₂O₈, which is ~ 0.3 M. The obtained results are shown in Figure 1. Surprisingly, H₂O₂ outperformed both NaOCl and K₂S₂O₈ by exhibiting a markedly higher initial dissolution rate under identical reaction conditions (see Table 1). This outcome can be explained by considering the dissolution reactions occurring in solution. In a pure carbonate solution, such as K₂CO₃, the following chemical reaction is known to predominate²⁸



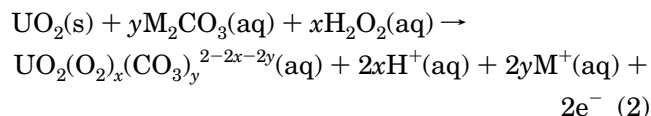
where (aq) and (s) indicate aqueous and solid phases, respectively. Indeed, when either NaOCl and K₂S₂O₈ was used as the oxidant, the uranyl triscarbonate tetraanion, UO₂(CO₃)₃⁴⁻, was formed. The presence of the yellow UO₂(CO₃)₃⁴⁻ solution species was confirmed spectrophotometrically by its characteristic absorbance

Table 1. Initial UO₂ Dissolution Rates as a Function of Different Reaction Parameters

carbonate concentration	oxidant concentration	initial dissolution rate ^a (% dissolved/min)
1.0 M K ₂ CO ₃	0.1 M H ₂ O ₂	1.7
1.0 M K ₂ CO ₃	0.1 M K ₂ S ₂ O ₈	0.3
1.0 M K ₂ CO ₃	0.1 M NaOCl	0.1
0.1 M Li ₂ CO ₃	0.7 M H ₂ O ₂	8.4
1.0 M K ₂ CO ₃	0.7 M H ₂ O ₂	11.2
1.0 M Na ₂ CO ₃	0.7 M H ₂ O ₂	14.2
1.0 M (NH ₄) ₂ CO ₃	0.7 M H ₂ O ₂	15.4
0.25 M K ₂ CO ₃	0.7 M H ₂ O ₂	13.3
0.5 M K ₂ CO ₃	0.7 M H ₂ O ₂	11.4
1.0 M K ₂ CO ₃	0.7 M H ₂ O ₂	11.2
2.0 M K ₂ CO ₃	0.7 M H ₂ O ₂	11.0
3.0 M K ₂ CO ₃	0.7 M H ₂ O ₂	5.5
5.0 M K ₂ CO ₃	0.7 M H ₂ O ₂	3.8
0.5 M Na ₂ CO ₃	0.04 M H ₂ O ₂	0.7
0.5 M Na ₂ CO ₃	0.07 M H ₂ O ₂	1.7
0.5 M Na ₂ CO ₃	0.17 M H ₂ O ₂	3.3
0.5 M Na ₂ CO ₃	0.35 M H ₂ O ₂	7.5
0.5 M Na ₂ CO ₃	0.70 M H ₂ O ₂	15.8
0.5 M Na ₂ CO ₃	3.50 M H ₂ O ₂	20.1

^a Rates were determined using 170 mmol of UO₂.

bands at 435, 448, and 462 nm (Figure 2A). In contrast, addition of H₂O₂ as the oxidant produced a red solution, which suggests that peroxide not only catalyzes the oxidation of uranium but also coordinates the uranium metal center under alkaline conditions. Interestingly, nearly 60 years ago, Na₂CO₃ and H₂O₂ were added to acidic UO₂²⁺ solutions to produce a red solution complex for colorimetrically determining the molar concentration of U(VI).^{40,41} However, the solution complex proposed at that time was incorrect because of the absence of carbonate groups. A general reaction that more accurately describes the solution speciation from the dissolution of UO₂ in the presence of pure carbonate and peroxide is



where M⁺ denotes an alkali metal cation and *x* and *y* are the molar stoichiometries of H₂O₂ and CO₃²⁻, respectively.

To determine the effect of varying peroxide concentration on solution speciation, a spectrophotometric titration was performed. The results obtained are shown in Figure 2A. The starting solution consisted of 2 mM UO₂(CO₃)₃⁴⁻. Hydrogen peroxide was incrementally titrated into the uranyl triscarbonate solution, resulting in distinct changes in the absorption spectrum. The characteristic peak maxima of UO₂(CO₃)₃⁴⁻ at 448 nm and 462 nm slowly disappeared with increasing peroxide concentrations, resulting in a rather nondescript absorption spectrum related to U(VI) peroxocarbonate complex formation. This finding suggests that peroxide is a facile ligand capable of displacing carbonate under alkaline conditions. The final concentration of peroxide was approximately 2 mM, which corresponds to possible uranium-to-peroxide mole ratios of 1:1, 2:2, 3:3, etc. in the solution complex.

Because the H₂O₂/U(VI) mole ratio changes during the UO₂ dissolution process as a result of uranium coordination and peroxide decomposition in carbonate media, several U(VI) peroxocarbonate species might exist in equilibrium. Therefore, experiments were performed that varied the dissolved uranium concentration

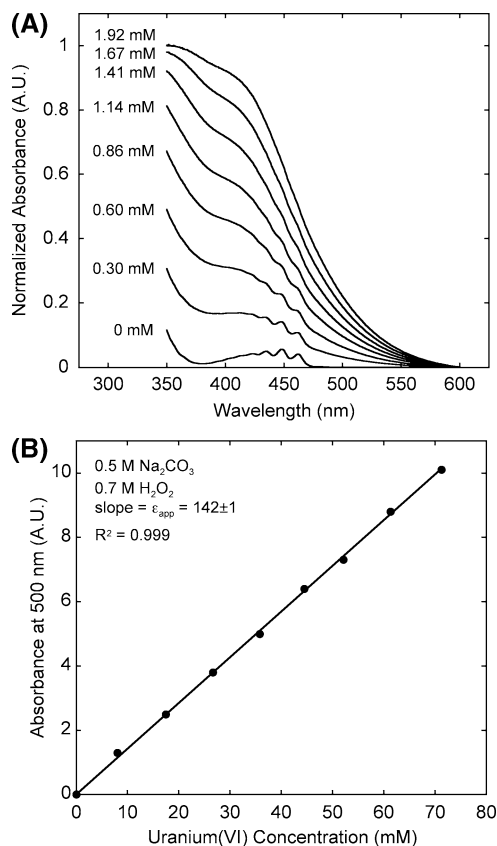


Figure 2. (A) Normalized UV-visible absorbance spectra illustrating the effect of increasing peroxide concentration on the solution speciation of U(VI) in an aqueous carbonate system. The U(VI) solution species in the absence of peroxide was 2 mM UO₂(CO₃)₃⁴⁻. (B) Molar extinction coefficient (500 nm) of the red peroxocarbonate solution complex over the entire uranium concentration range (0–70 mM) studied.

from 0 to 70 mM under fixed concentrations of 0.5 M Na₂CO₃ and 0.7 M H₂O₂. The results are shown in Figure 2B. The absorbance values shown have been extrapolated from samples diluted in 0.5 M Na₂CO₃. The linearity of the data in Figure 2B indicates that only one U(VI) solution species is present after dilution to concentrations that obey the Beer-Lambert law. The molar extinction coefficient of this uranyl(VI) peroxocarbonate species was determined to be 142 ± 1 at 500 nm (see Experimental Section). It should be emphasized that the molar extinction coefficient reported corresponds to the solution species that exists after dilution in 0.5 M Na₂CO₃, which may not be the same species present in the original solution following dissolution. Single-crystal X-ray analysis of a precipitate formed from a uranyl(VI) peroxocarbonate solution identified a molecular mononuclear U(VI) structure, K₄UO₂(O₂)(CO₃)₂, with the peroxide and carbonate ligands bidentately coordinated in the equatorial plane to the U(VI) metal center.⁴² Similar binding geometries have been reported for another uranium(VI) peroxocarbonate compound,⁴³ as well as for lanthanide peroxocarbonates.^{44,45} These structural data, in conjunction with the data shown in Figure 2B, suggest that the solution species present 4 h after dissolution has the composition UO₂(O₂)(CO₃)₂⁴⁻.

After selecting H₂O₂ as the oxidizing agent for dissolving UO₂, several reaction parameters were evaluated in order to optimize the dissolution process, including carbonate concentration, carbonate counter-cation, and peroxide concentration. Figure 3A shows the

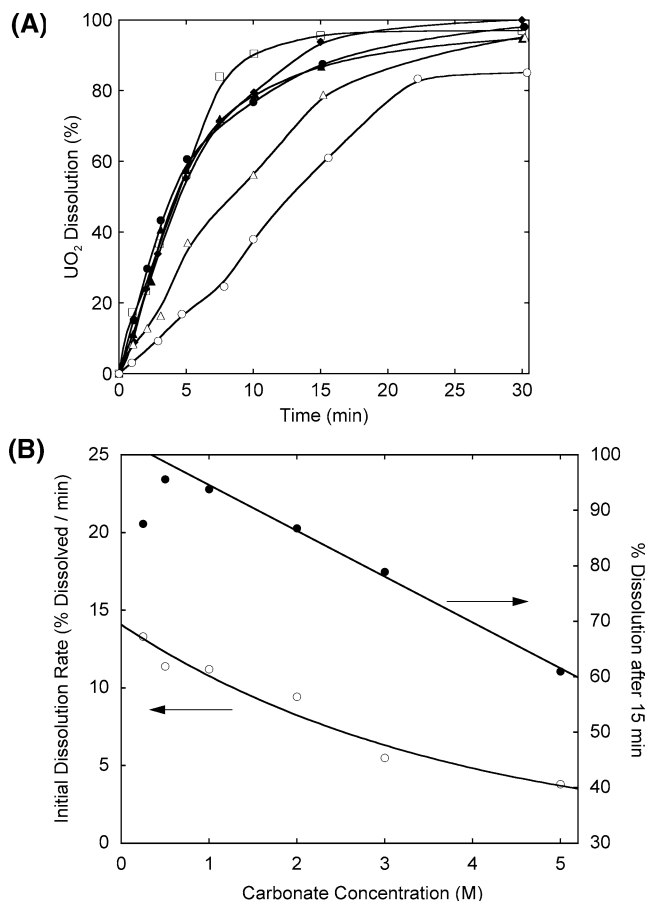


Figure 3. (A) Effect of K_2CO_3 concentration on the dissolution behavior of UO_2 powder. Reactant concentrations were (●) 0.25, (□) 0.5, (◆) 1.0, (▲) 2.0, (△) 3.0, and (○) 5.0 M carbonate; 70 mM UO_2 ; and 0.7 M H_2O_2 . (B) Dependence of the initial UO_2 dissolution rate and the dissolution capacity after 15 min on the carbonate concentration. Solid lines indicate exponential and linear trends in the data.

dissolution behavior of UO_2 in 0.25–5 M potassium carbonate solutions, and the initial dissolution rates and dissolution capacity are illustrated in Figure 3B. It is apparent from Figure 3 that 0.25 M carbonate exhibits the highest initial rate of UO_2 dissolution (see Table 1). Furthermore, as the carbonate concentration increases, the dissolution rate shows an exponential decrease. This might be due to either the effects of increased ionic strength or an increased rate of H_2O_2 degradation. Nonetheless, to maximize the efficiency of the dissolution process, the dissolution capacity must also be considered. Figure 3B demonstrates that 0.5 M carbonate dissolves the highest amount of UO_2 , followed by a nearly linear decrease as a function of increasing carbonate concentration. Interestingly, at 0.25 M carbonate concentration, the dissolution capacity does not exceed 85% within 15 min. This is most likely due to the decreasing concentration of free carbonate in solution, which appears to become rate limiting at this point. Judging from the initial dissolution rate and the overall dissolution efficiency demonstrated in Figure 3 and Table 1, the optimal carbonate concentration was determined to be 0.5 M, with nearly 85% of the UO_2 (40 mg total) being dissolved within 7 min. The carbonate concentration also plays an important role in dictating the solubility of the uranyl peroxocarbonate solution species. At carbonate concentrations between 0.5 and 1.0 M, the peroxocarbonate species remains in solution indefinitely, whereas at concentrations below 0.5 M

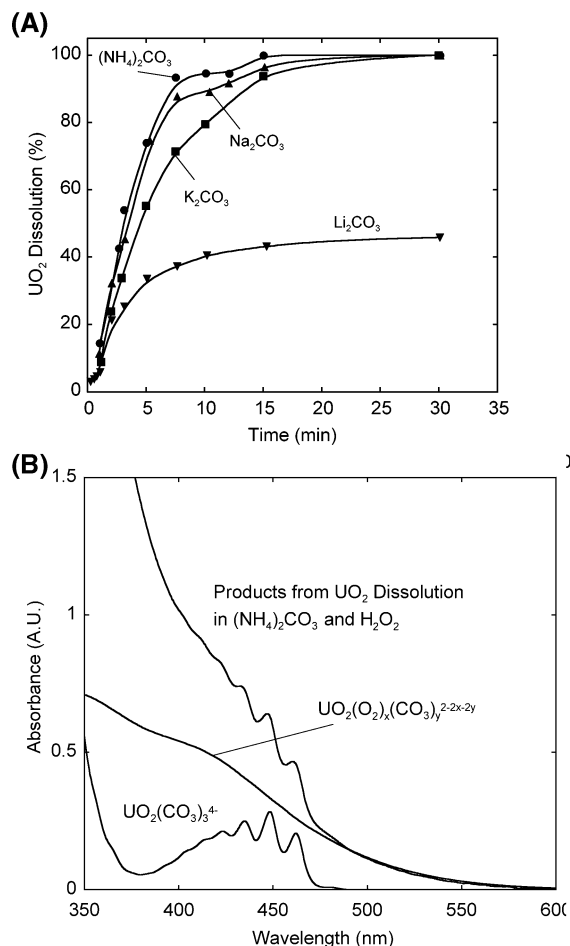


Figure 4. (A) Carbonate counteranion dependence on the dissolution behavior of UO_2 in the presence of peroxide. The Li_2CO_3 dissolution data was obtained using a 0.1 M solution, whereas the data for K_2CO_3 , Na_2CO_3 , and $(\text{NH}_4)_2\text{CO}_3$ were obtained using 1.0 M solutions. (B) UV-visible absorbance spectra of $\text{UO}_2(\text{CO}_3)_3^{4-}$ (in the absence of peroxide) and two representative absorbance spectra generated from the dissolution of UO_2 in hydrogen peroxide solutions containing ammonium or alkali metal carbonate counteranions.

carbonate and between 1 and 3.0 M carbonate, a yellow amorphous precipitate forms after a few weeks. At the present time, this product has not been characterized. At carbonate concentrations at or above 5.0 M, yellow-orange crystals precipitate after a few days. Single-crystal X-ray diffraction has determined the composition to be $\text{K}_4\text{UO}_2(\text{CO}_3)_3$ (data not shown). The solubility and characterization of resultant precipitates and solution species will be important for designing a new head-end SNF reprocessing approach. Furthermore, the determination of fission product decontamination factors will also be requisite for process development.

In addition to carbonate concentration, another variable that has a substantial impact on both the initial dissolution rate and the dissolution efficiency is the carbonate counteranion. Preliminary experiments focused on 0.1 M carbonate salts of Li^+ , Na^+ , K^+ , Cs^+ , and NH_4^+ ; however, Cs^+ was not used in subsequent studies because the presence of this carbonate counteranion yielded a gelatinous UO_2 dissolution product. Among the other cations studied the following trend in dissolution efficacy was observed: $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{NH}_4^+$ (data not shown). A typical dissolution curve using 0.1 M Li_2CO_3 is shown in Figure 4A. One disadvantage associated with using Li_2CO_3 is that it has a rather poor

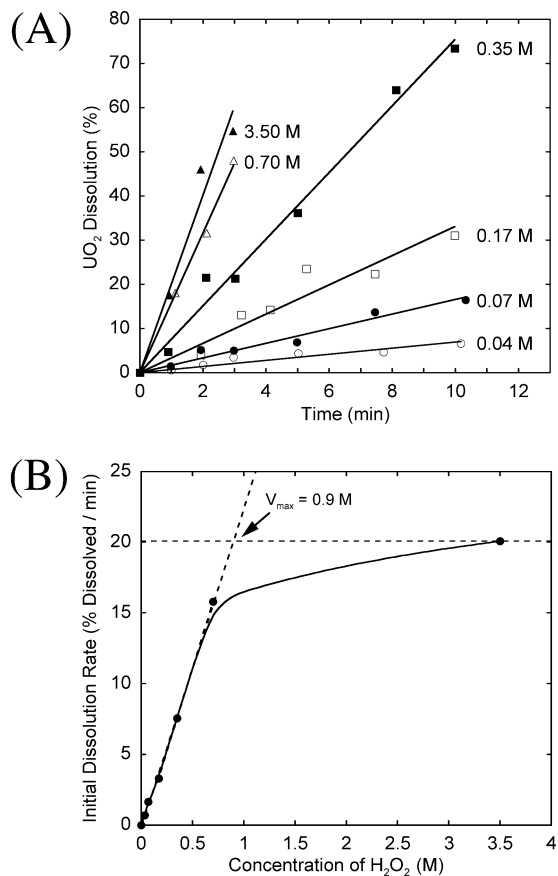


Figure 5. (A) Effect of hydrogen peroxide concentration on the dissolution behavior of UO_2 in 0.5 M Na_2CO_3 . Solid lines indicate the region over which initial dissolution rates were calculated. (B) Determination of the optimum hydrogen peroxide concentration for dissolving UO_2 most rapidly. Initial dissolution rates were taken from the data in part A.

solubility of ~ 0.18 M; therefore, it was not used in later studies. Figure 4A also depicts the dissolution behavior of UO_2 in 1.0 M $(\text{NH}_4)_2\text{CO}_3$, Na_2CO_3 , and K_2CO_3 . A summary of the initial UO_2 dissolution rates can be found in Table 1. Both $(\text{NH}_4)_2\text{CO}_3$ and Na_2CO_3 behave quite similarly, showing a noticeable improvement over the performance of K_2CO_3 . A distinct difference between $(\text{NH}_4)_2\text{CO}_3$ and Na_2CO_3 , however, is apparent in the resultant absorption spectra recorded after the dissolution (Figure 4B). The absorption spectrum of the peroxocarbonate complex, shown in Figure 4B, is consistent with those of other uranyl peroxocarbonate species reported,^{46,47} but it is significantly different from the absorbance of $\text{UO}_2(\text{CO}_3)_3^{4-}$. It is evident from Figure 4B that the solution speciation associated with the dissolution of UO_2 in $(\text{NH}_4)_2\text{CO}_3$ is substantially different from that observed in alkali metal carbonates. It is plausible that a mixture of $\text{UO}_2(\text{O}_2)_x(\text{CO}_3)_y^{2-2x-2y}$ and $\text{UO}_2(\text{CO}_3)_3^{4-}$ are in equilibrium in this solution of $\text{pH} \approx 10$ (whereas in an alkali metal carbonate solution the pH is ~ 12). This shift in equilibrium toward the formation of a higher mole fraction of $\text{UO}_2(\text{CO}_3)_3^{4-}$ can be explained by the pK_a values, with $\text{pK}_a(\text{H}_2\text{O}_2) = 11.7$ and $\text{pK}_a(\text{NH}_4^+) = 9.2$.⁴⁸ In the less alkaline $(\text{NH}_4)_2\text{CO}_3$ solution, less of the OOH^- ligand is present, whereas a higher concentration of HOOH exists, which will shift the equilibrium away from the formation of a uranyl peroxocarbonate complex.

Because of the significant impact that peroxide imparts to the UO_2 dissolution process, it was necessary

to study the effects of varying peroxide concentration on the dissolution behavior of UO_2 (see Figure 5A). Several uranium-to-peroxide mole ratios were investigated, namely, 1:0.5, 1:1, 1:2.5, 1:5, 1:10, and 1:50, which corresponded to peroxide concentrations of 35, 70, 170, 350, and 700 mM and 3.50 M, respectively. Initial dissolution rates were calculated from the linear regions of the resultant dissolution curves (see Table 1). By extrapolating the linear response range to the point at which it intersects the maximum dissolution rate, the peroxide concentration with the fastest dissolution kinetics was estimated to be 0.9 M (see Figure 5B).

Conclusion

The dissolution of UO_2 powder in aqueous oxidative carbonate solution was investigated. Several oxidizing agents were screened, with hydrogen peroxide exhibiting the best overall performance. Reaction parameters, including carbonate concentration, carbonate counter-cation, and hydrogen peroxide concentration, were studied and optimized, with 0.5 M Na_2CO_3 and 0.9 M H_2O_2 yielding the highest dissolution rates and highest dissolution efficiency for 170 mmol of UO_2 . The kinetic data and solution complexation reactions presented herein will aid in the development of a new process for dissolving SNF in nonacidic media.

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