



Effects of the different conditions of uranyl and hydrogen peroxide solutions on the behavior of the uranium peroxide precipitation

Kwang-Wook Kim*, Jun-Taek Hyun, Keun-Young Lee, Eil-Hee Lee, Kune-Woo Lee, Kee-Chan Song, Jei-Kwon Moon

Korea Atomic Energy Research Institute, 1045 Daedeok daero, Yuseong, Daejeon, 305-353, Republic of Korea

ARTICLE INFO

Article history:

Received 18 October 2010

Received in revised form 2 July 2011

Accepted 7 July 2011

Available online 18 July 2011

Keywords:

Uranium peroxide
Hydrogen peroxide
Uranyl ion
Induction time
Precipitation

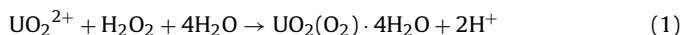
ABSTRACT

The dynamic precipitation characteristics of UO_4 in different solution conditions (pH, ionic strength, uranium and H_2O_2 concentrations) were characterized by measuring changes in the absorbance of the precipitation solution and by monitoring the change of particle size in a circulating particle size analyzer. The precipitation solution conditions affected the precipitation characteristics such as the induction time, precipitation rate, overall precipitation time, and particle size in a complex manner. With increases in both pH and ionic strength, the induction time was prolonged, and the individual particle size decreased, but the individual particles tended to grow by aggregation to form larger precipitates. The uranium concentration and the ionic strength of the solution affected the induction time and precipitation rate to the greatest extent.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Uranium minerals such as uranium peroxide hydrates studtite ($\text{UO}_4 \cdot 4\text{H}_2\text{O}$) and metastudtite ($\text{UO}_4 \cdot 2\text{H}_2\text{O}$) are known to form on spent nuclear fuel when stored in a disposal repository by the incorporation of peroxide formed by the alpha radiolysis of water [1–4]. These uranium peroxide hydrates can also be synthesized by adding excess hydrogen peroxide (H_2O_2) to an acidic solution of uranyl ions [1,5–7], as shown in Eq. (1).



The uranium peroxide hydrates are the only known peroxide-bearing minerals and have very low solubilities, in the order of 10^{-3} – 10^{-5} M [1,2,7,8]. Therefore, the precipitation of UO_4 is highly selective for uranium in most solutions and, with proper control, can produce a crystalline and easily handled product [9]. Accordingly, methods for dissolving uranium-bearing materials in acid followed by the precipitation of uranyl ion (UO_2^{+2}) as UO_4 by the addition of H_2O_2 to the acidic uranium solution have been developed for the recovery of uranium from uranium ore and uranium scraps or for waste treatment, e.g., of a uranium-contaminated solution [5,10,11]. Recently, a carbonate-based process has been introduced, where uranium from spent nuclear fuel is selectively

leached in the form of a uranyl peroxo carbonate complex ion ($\text{UO}_2(\text{O}_2)_x\text{CO}_3^{y-2}$) in a carbonate solution containing H_2O_2 and the uranium complex ion is subsequently recovered as a precipitate of UO_4 by acidifying the carbonate solution [11].

The precipitation of UO_4 is known to be dependent on pH, temperature and the presence of other ions in the solution. However, its precipitation behavior has not yet been fully elucidated, and the data on the precipitation conditions are very scanty. In our preliminary experiments with this system, the precipitation behavior of UO_4 was found to be complicated and dependent on solution conditions. In this work, changes in the UO_4 precipitation characteristics such as induction time (the time before the precipitation begins), precipitate size, and precipitation rate were investigated by changing several solution conditions.

2. Experimental

The precipitation of UO_4 was performed by adding uranyl nitrate ($\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) in H_2O_2 solutions at concentrations in the range of 0.5–3 M to make final uranium concentrations in the range of 500–5000 ppm and adjusting these with HNO_3 and NaOH to pH values between 0.5 and 3, and with NaNO_3 to ionic strengths between 0.5 and 3 M. The precipitation experiments were performed either in a 1 cm cuvette held in a UV–vis spectrophotometer (HP 8453) without any agitation in the cuvette, and the parallel experiments with the same conditions as those in the spectrophotometer were carried out in the circulating sample holder of a particle size ana-

* Corresponding author. Tel.: +82 42 868 2044; fax: +82 42 868 2351.
E-mail address: nkwkim@kaeri.re.kr (K.-W. Kim).

lyzer (Microtrac S3000) with detection lime of more than 0.1 μm to directly measure and monitor the dynamic precipitation behavior and the precipitate characteristics in the solutions. The induction period for precipitation and the duration of precipitate suspension were evaluated by monitoring the absorbance of the precipitation solution [12]. By measuring the changes in absorbance and the actual particle size distribution of the precipitate in the solution with time, the dynamic behavior of UO_4 precipitation was analyzed in situ in several solution conditions.

After precipitation, the UO_4 precipitate was washed with demineralized water and then analyzed by XRD (Rigaku, Cu $K\alpha$), SEM (PerkinElmer), TEM (Tecnai F20) for ex situ evaluation. The uranium concentration in the supernatant after the precipitation was analyzed to evaluate the precipitation yield of uranium as UO_4 in the solution using a colorimetric method with Arsenazo III [13]. All the reagents used in this work were of reagent grade, and they were dissolved, as received, in demineralized water prepared by a double distillation followed by an ion-exchange (Milli-Q plus; 18.2 $\text{M}\Omega$). All the experiments were performed at room temperature.

3. Results and discussion

We investigated the changes in the UO_4 precipitation-behavior characteristics with different solution conditions. Therefore, before describing the experimental results on the precipitation characteristics of UO_4 , herein follows a brief introduction to the general process of the formation of particles from a solution. Particles are generated by nucleation followed by the growth of the solid phase to form particles of visible size. Nucleation is generally described as the formation of dispersed nuclei from a homogeneous supersaturated phase. In the process of precipitation, the first step is the formation of clusters by the coagulation of dissolved molecules or solvated ions in solution; next, nucleation occurs by the formation of dispersed nuclei from the clusters in the solution [15]. There may be an induction period before the detection of the first crystal or solid particles. Once nuclei occur, particles grow in two ways. The first is particle growth by agglomeration, with a gradual building up of layers of material on the surface of seeds by the molecular diffusion of species to form a collection of particles held together by strong interparticle forces. The second mechanism is particle growth by aggregation due to the collision and subsequent joining of two or more particles of similar sizes with weak cohesive forces. However, the classification of detailed mechanisms of nucleation and particle growth is difficult and is lacking for many systems [14,15].

To directly monitor and measure the dynamic precipitation characteristics of UO_4 in solution, we analyzed the absorbance changes in UO_4 precipitation solutions and related these results to its precipitation behavior. The changes in the absorbance spectra and particle size distributions with time in a 500 ppm uranium solution at 1.0 M H_2O_2 , pH 1, and an ionic strength of 0.5 M were independently measured by using a spectrophotometer and a solution-circulating particle size analyzer; the results are shown in Figs. 1 and 2, respectively. The uranium solution prepared for this experiment was yellowish and had an initial absorption peak at ~ 353 nm. As shown in Fig. 1, the overall absorbance increased with time during the UO_4 precipitation. The absorbance spectrum began to display significant fluctuations after about 30 min, particularly at wavelengths less than 325 nm. The initial solution became turbid, indicating particle suspension in the solution without precipitation before 30 min, after which visible particles were observed in the solution, and particles larger than 0.1 μm were also detected by the particle size analyzer; the particle size distribution then stabilized and approached a constant value with time. As the precipitate settled out of the solution, the absorbance amplitude of the spec-

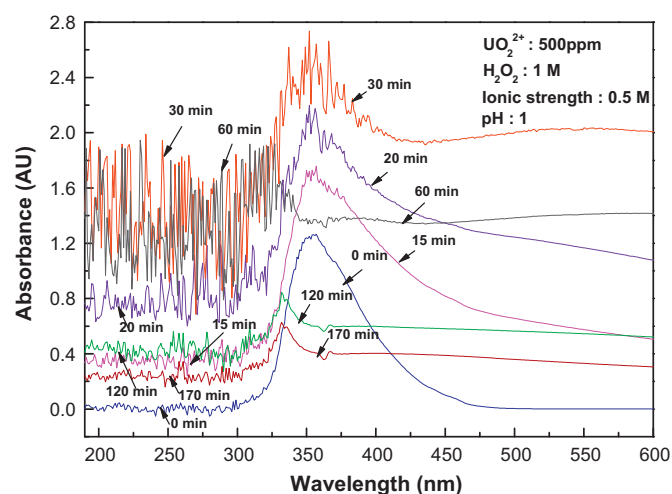


Fig. 1. Change of the absorbance spectrum with time in a uranium solution of 500 ppm at 1.0 M H_2O_2 , pH 1, and an ionic strength of 0.5 M.

trum gradually decreased and the fluctuations gradually subsided. Finally, the absorbance peak at 353 nm disappeared at the end of the precipitation and the solution became transparent. However, the final absorbance remained at a non-zero value because the fine UO_4 particles, which occurred in the solution during the precipitation, were still attached to the inside wall of the cuvette in the spectrophotometer at the end of precipitation. The absorbance of the solution after the complete precipitation was confirmed to be zero in a fresh cuvette, because all the uranyl ions in the previous cuvette were precipitated as UO_4 in the solution, although this result is not present in this work. Fig. 3 shows the changes of absorbance at 325 nm and the mean particle sizes from Figs. 1 and 2 on the same plot. The wavelength of 325 nm was chosen because the absorbance change during the precipitation was the greatest at that wavelength, as shown in Fig. 1. The absorbance remained constant for a time at the beginning of the precipitation, rose to a maximum, and finally decreased and stabilized at a low absorbance value. The mean particle sizes shown in Fig. 3 are the mean volume diameter, which is the value calculated as a diameter of a hypothetical sphere with a volume equivalent to the measured nonspherical particle. The time at which the maximum absorbance during the precipitation occurred, ~ 30 min, nearly coincided with the time at which the first particles larger than 0.1 μm were detected by the particle size

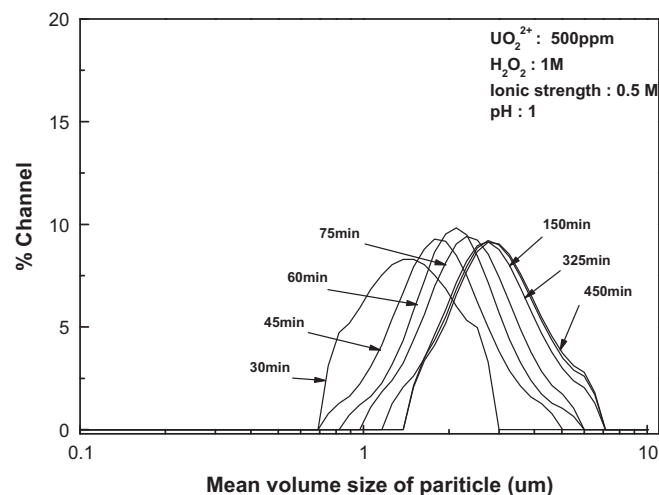


Fig. 2. Changes in the particle size distributions with time in a 500 ppm uranium solution at 1.0 M H_2O_2 , pH 1, and an ionic strength of 0.5 M.

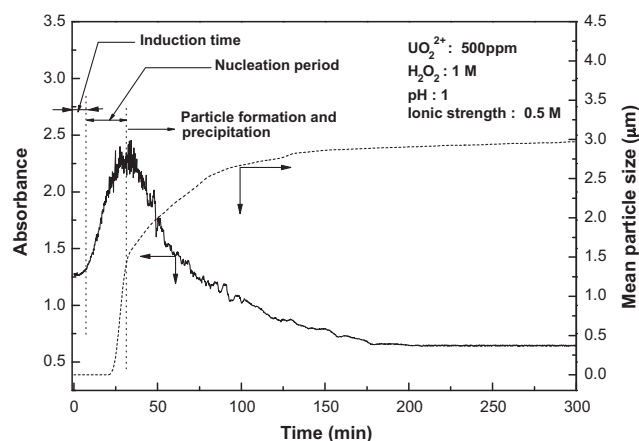


Fig. 3. Changes of absorbance at 325 nm and mean volume diameter of the particles with time in a UO_4 precipitation solution from Figs. 1 and 2.

analyzer. The particle size gradually increased with the precipitation time and approached a final, stable size of approximately $3 \mu\text{m}$ after 150 min. In view of the precipitation steps described above, the first period with no change of absorbance is considered to be due to the induction time, during which the formation of clusters by the coagulation of dissolved molecules or solvated ions occurred, but any particles affecting the absorbance are not yet formed during this time. The second period, in which the absorbance increased and reached the maximum, is considered to be due to the onset of nucleation by the formation of dispersed nuclei from the clusters in the solution. Therefore the solution becomes turbid and the absorbance increases, but the particles to be precipitated do not appear in the solution, and the nuclei are not detected by the particle size analyzer with detection limit of more than $0.1 \mu\text{m}$ yet because they are still too small. After the absorbance reaches the maximum, as the suspended nuclei grow and form bigger particles, the particles begin to settle down into the solution and the solution absorbance begins to decrease because the solution gradually becomes transparent due to the settling of the particles from the solution. From then on, the particles in the solution are observed by the particle size analyzer, and the particle size increases further and the precipitation is facilitated. Fig. 4 presents SEM micrographs of UO_4 particles precipitated at 50, 180, and 240 min, showing that the particles grew with precipitation time. The form of the precipitated particles resembles two cones joined at their bottoms. The actual mean volume diameters of the particles was calculated from the particle dimensions in the photomicrographs; they were 2.1, 2.8, and $3.1 \mu\text{m}$ at 50, 180, and 240 min, respectively, which are very similar to those measured by the particle size analyzer (see Fig. 3). Based on these results, the simultaneous measurements of the absorbance pattern at a constant wavelength and particle size in the precipitation solution appears to be an effective tool for evaluating several precipitation characteristics such as the induction time, nucleation and precipitation rates (slopes of absorbance changes), overall precipitation time, and particle size. Fig. 5 shows the XRD result of the precipitate obtained after 240 min in Fig. 4, which was washed with water and dried at 90°C . It was identified as $\text{UO}_4 \cdot 2\text{H}_2\text{O}$. When UO_4 precipitate is dried below and above 70°C , UO_4 is known to exist in the form of $\text{UO}_4 \cdot 4\text{H}_2\text{O}$ (studtite) and $\text{UO}_4 \cdot 2\text{H}_2\text{O}$ (meta studtite), respectively [15]. All the XRD results of the other uranium precipitates obtained at the different conditions in this work were all UO_4 hydrates the same as Fig. 5, although they are not present in this manuscript. In these experiments, we confirmed that after the UO_4 precipitation occurred in the solutions under the various conditions, the precipitation yields in all cases, as determined by measuring uranium concentrations in the super-

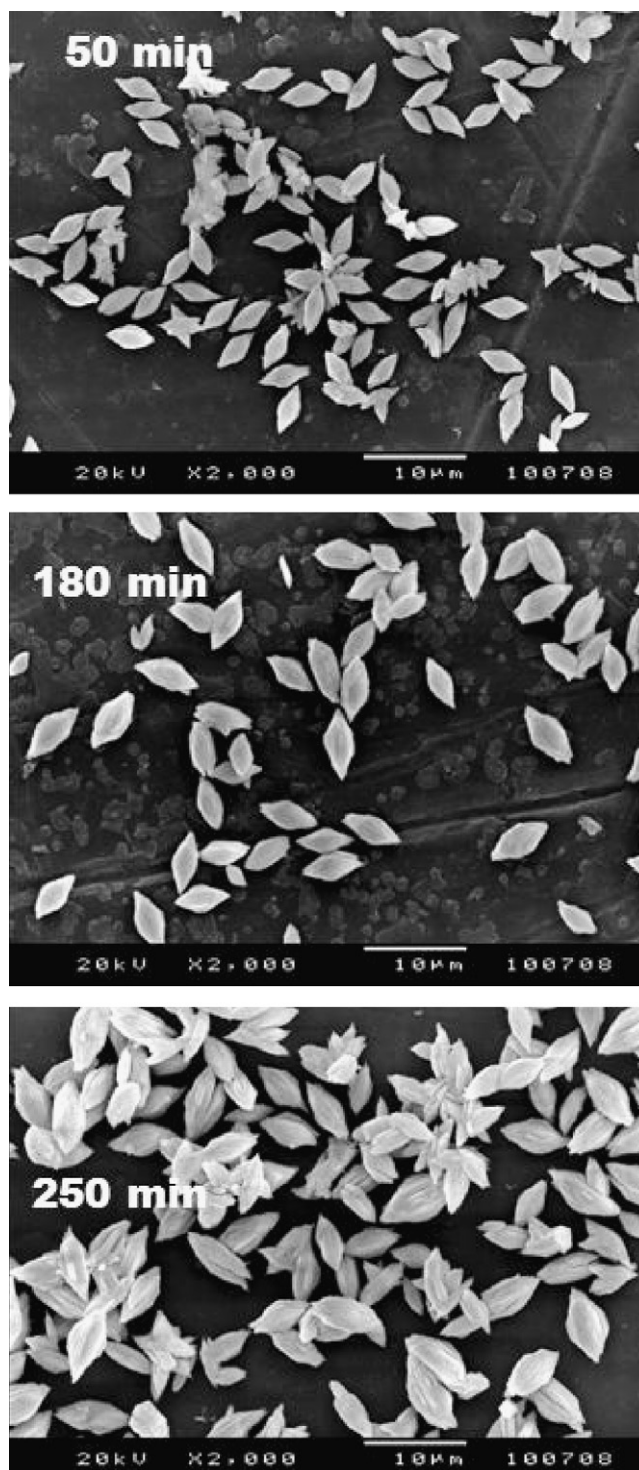


Fig. 4. SEM photographs of UO_4 particles precipitated at 50, 180, and 240 min in a 500 ppm uranium solution at 1.0 M H_2O_2 , pH 1, and an ionic strength of 0.5 M.

natant after precipitation, were over 99%; this was as expected because the solubility of UO_4 is very low [1,2,7,8]. Therefore, the precipitation yield does not merit further discussion.

Fig. 6 shows the changes in the absorbance and mean volume diameter of the particles with time in 500 ppm uranium solutions at 1.0 M H_2O_2 , ionic strength 0.5 M, and various pH values. When the solution pH increased, the induction time also increased. However, the absorbance rising slope, which means the nucleation rate, and the time at which the precipitation began (the time the absorbance

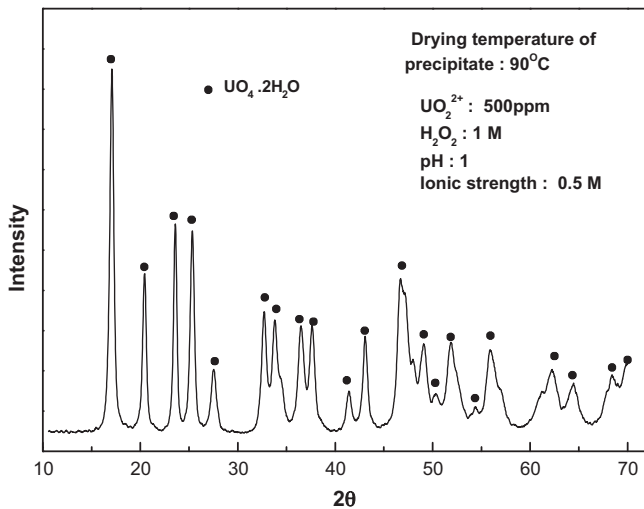


Fig. 5. XRD spectrum of the uranium precipitate dried at 90°C.

reached the maximum) decreased. The particle size decreased with an increase in solution pH. It was interesting to observe that the particle sizes at pH 2 and 3 gradually increased in the solution over time even after the precipitation reaction finished. The phenomenon was likely due to particle growth by aggregation due to the collision and joining of two or more particles in the circulating solution in the particle size analyzer. Fig. 7 shows the SEM micrographs of particles precipitated at pH 2 and 3 after 240 min, at which the absorbance change reached the minimum and remained constant, indicating that the precipitation reaction itself in the solution was already finished. A number of big aggregated particles are observed, even though the individual particles composing of the aggregated particles are small, at around 1 μm , which is quite different from the case at pH 1, as shown in Fig. 4. These results suggest that the individual particles generated in the solution are prone to aggregation, forming larger precipitates at higher pH values.

Fig. 8 shows the changes in the absorbance and mean volume diameters of the particles with time in 500 ppm uranium solutions at pH 1, 1.0 M H_2O_2 , and various ionic strengths. The UO_4 precipitation occurred immediately, without an induction time, at 0.1 M ionic strength, and the generated particles showed a constant and stable size over the entire precipitation time. However, the induction time and precipitation time were prolonged with increases

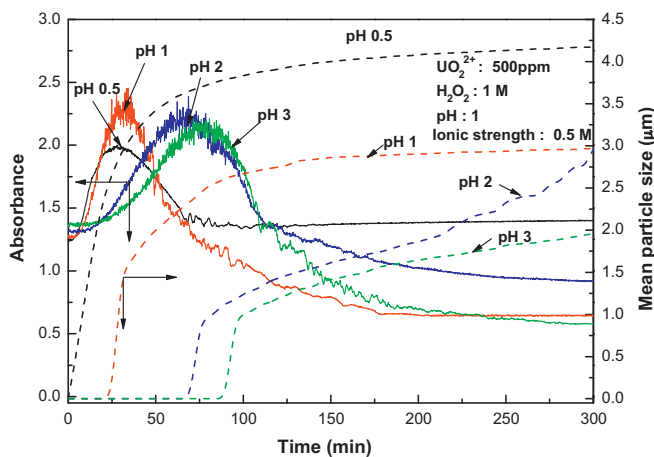


Fig. 6. Changes in the absorbance and mean volume diameter of the particles with time in 500 ppm uranium solutions at 1.0 M H_2O_2 , an ionic strength of 0.5 M and several solution pH values.

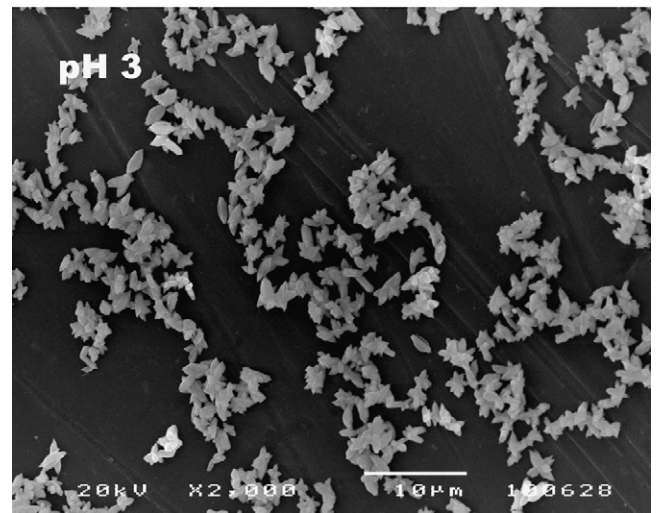
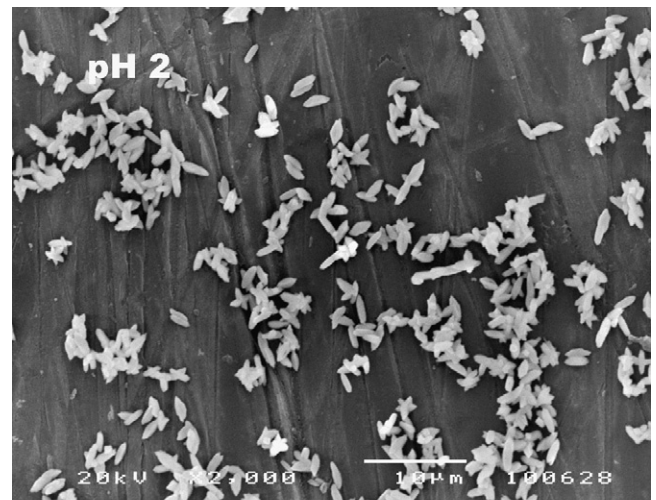


Fig. 7. SEM micrographs of UO_4 particles precipitated at 240 min in a 500 ppm uranium solution at 1.0 M H_2O_2 , an ionic strength of 0.5 M, and pH 2 and 3.

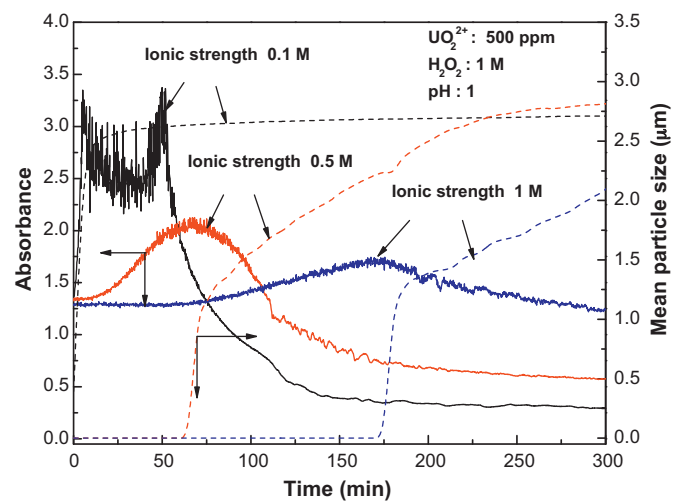


Fig. 8. Changes in the absorbance and mean volume diameter of the particles with time in 500 ppm uranium solutions at 1.0 M H_2O_2 , pH 1, and several solution ionic strengths.

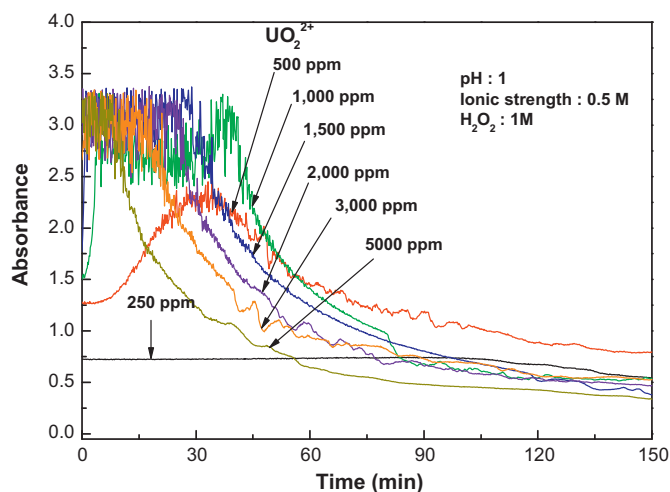


Fig. 9. Changes in the absorbance with time in uranium solutions at 1.0 M H_2O_2 , pH 1, ionic strength 0.5 M, and several uranium concentrations.

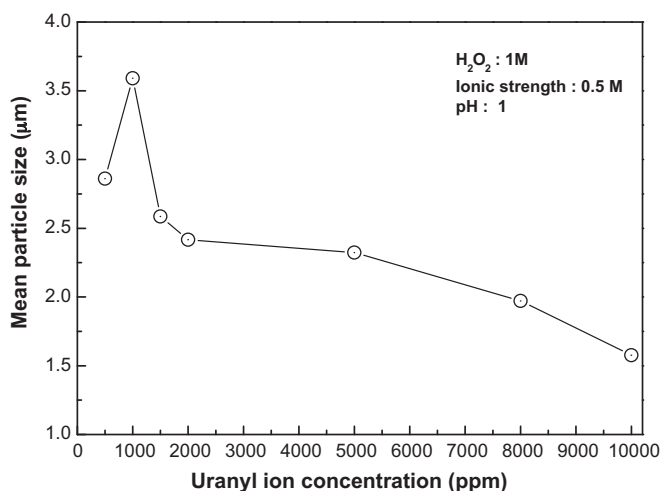


Fig. 10. Changes of the mean volume diameter of the particles generated at 240 min in uranium solutions at 1.0 M H_2O_2 , pH 1, and ionic strength 0.5 M with several uranium concentrations.

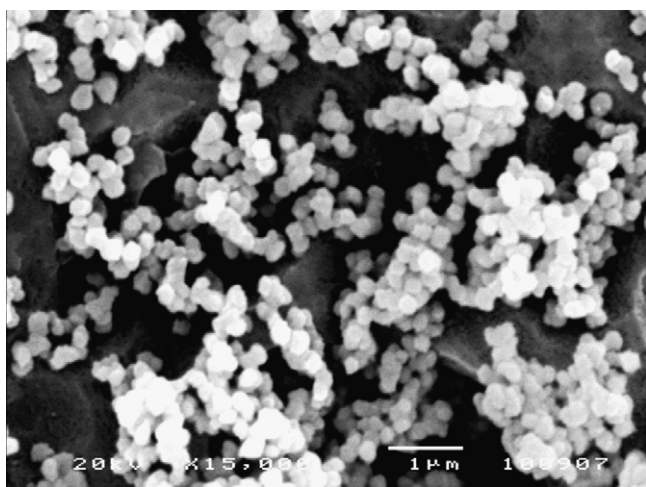


Fig. 11. SEM micrographs of UO_4 particles precipitated at 240 min in a 5000 ppm uranium solution at 1.0 M H_2O_2 , ionic strength 0.5 M, and pH 1.

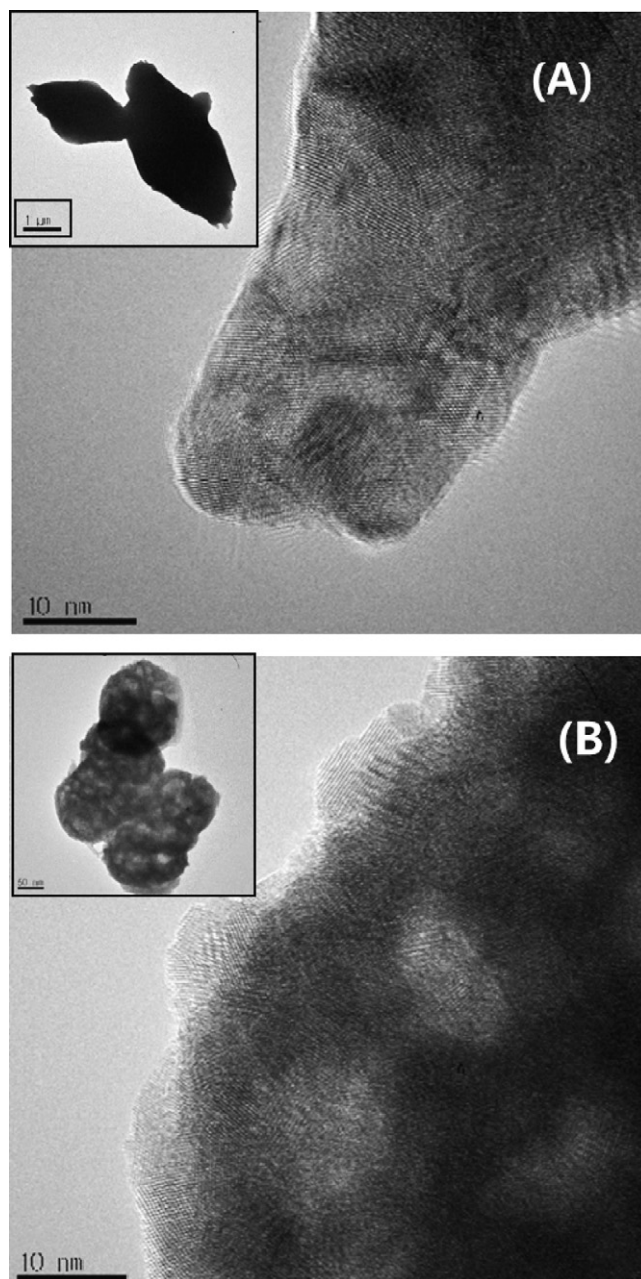


Fig. 12. TEM micrographs of UO_4 single particles of precipitates generated at 240 min in 500 ppm (A) and 5000 ppm (B) uranium solutions at 1.0 M H_2O_2 , ionic strength 0.5 M, and pH 1.

in ionic strength, and the particle size showed a pattern of steady growth due to the aggregation of individual particles, as discussed in the cases of pH 2 and 3 (Fig. 6). A higher ionic strength in solution at a constant uranium concentration means that the solution contains more anions and cations other than the uranium ions to be precipitated in the solution. Accordingly, the results of Fig. 8 indicate that the UO_4 precipitation was greatly affected by the presence of coexisting ions in the solution.

Fig. 9 shows the changes in absorbance with time in several uranium concentration solutions at 1.0 M H_2O_2 , pH 1, and ionic strength 0.5 M. Fig. 10 shows the change in the mean volume diameter of the particles generated in the solutions at the conditions of Fig. 9 at 240 min, at which the particle size became stable, as in the case of pH 1 in Fig. 6. When the uranium concentration was very low, as in the case of the 250 ppm solution, the absorbance peak

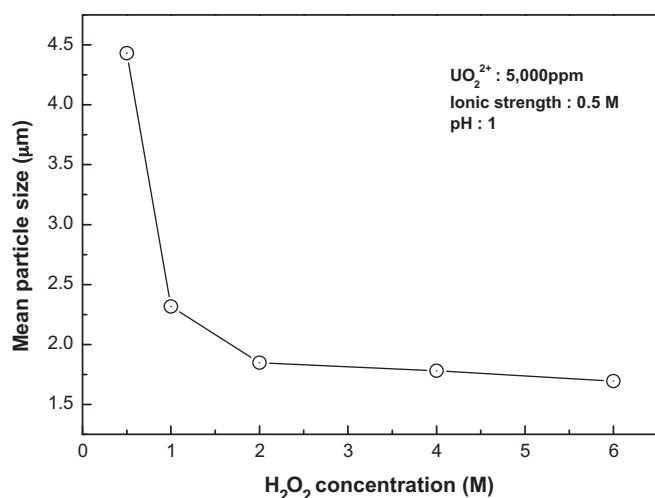


Fig. 13. Changes in the mean volume diameter of the particles generated at 240 min in 5000 ppm uranium solutions at pH 1, and ionic strength 0.5 M with various H₂O₂ concentrations.

was unclear and the induction time was very long. However, the precipitation of UO₄ did eventually occur. Conversely, when the uranium concentration was increased in the solution, the induction time and entire precipitation time were shortened and the precipitation rate rapidly increased. Thus the precipitation of UO₄ occurred almost immediately without induction at a uranium concentration of more than 2000 ppm. One interesting thing to note is that the increase in particle size showed a peak at the uranium concentration of 1000 ppm, but it then gradually decreased with increasing uranium concentration in the solution. Fig. 11 shows an SEM micrograph of the precipitate at the uranium concentration of 5000 ppm in Fig. 10. The precipitate is agglomeration of individual particles of ~0.15 µm in diameter, which look like round shape with irregular edges. This morphology was quite different from that generated in the same solution conditions except for the uranium concentration of 500 ppm in Fig. 4. The single particle in Fig. 4 had ~5 µm in longitudinal size and a shape with two cones joined at their bottoms, as mentioned above. To investigate that how the seed particles that initiate nucleation for the single particle of precipitates in Figs. 4 and 11 affect the final morphologies of the precipitates, the TEM micrographs of each precipitate generated at uranium concentration of 500 ppm and 5000 ppm in Figs. 4 and 11 were measured, and their results are shown in Fig. 12. The respective TEM micrographs were measured at the edge parts of single particles of the precipitates to observe clear seed particles of the single particle. Overall shapes of the single particles, which were measured in a low magnification, are shown in the inset boxes in Fig. 12. The seed particles are observed as an area with a line pattern in the same direction, which is due to interplanar distance of crystal, although they are overlaid one another in the single particle. They are considered to be unit crystals consisting of a single particle. The seed particles of the both cases are almost the same in a few nanometers and have somewhat irregular round shapes. From these results, the final morphologies of UO₄ precipitates can be said to be different with the UO₄ precipitation condition, even though the unit crystal of the precipitates is similar. The shape and size of finally grown crystal particle is known to be able to be different according to precipitation conditions, especially crystal growth rate or degree of saturation of the species to be precipitated in the solution. Every element of surface of crystal is capable of a different change contributing to the growth of crystal particle, depending on thermodynamic driving force in the solution. Generally, the predominant crystal in pre-

cipitation solution is bush-like spherulite at high supersaturation and is needle-like individual form at low supersaturation [16–18]. As mentioned above, the precipitation rate in the dense uranium solution at the 5000 ppm in Fig. 9 was much faster than that in the diluted uranium solution at 500 ppm in Fig. 6. Therefore, the reason of the difference in morphology of the precipitates generated at uranium concentration of 500 ppm and 5000 ppm is considered to be ascribed to the difference of growth rate in the single UO₄ particle in the solutions with different uranium concentrations. The concentration of H₂O₂ was experimentally observed to have no distinct effects on the induction time or precipitation rate of UO₄ in the uranium solution; however, it did affect the particle size. Fig. 13 shows the change in particle size generated at 240 min in 5000 ppm uranium solutions at pH 1 and an ionic strength of 0.5 M with different H₂O₂ concentrations. The particle size of the UO₄ precipitate decreased with the concentration of H₂O₂ but became constant above 2 M.

4. Conclusions

The dynamic precipitation characteristics of UO₄ were evaluated by the in situ measurements of absorbance in the precipitation solution and mean precipitate size in a circulating particle size analyzer. The precipitation solution conditions of pH, ionic strength, uranium and H₂O₂ concentration interacted in the formation of UO₄ precipitate in a complex way and affected the precipitation characteristics of induction time, precipitation rate, overall precipitation time, and particle size. With increases in the pH and ionic strength, the induction time was prolonged, and the individual particle size decreased, whereas the individual particles tended to grow by aggregation at higher pH values and ionic strengths. Of all the solution conditions, the uranium concentration and ionic strength affected the induction time and precipitation rate the most significantly.

Acknowledgments

This work was supported by the Ministry of Education, Science and Technology (MEST) of the Republic of Korea under the nuclear R&D Project.

References

- [1] K.-A.H. Kutatko, K.B. Helean, A.N. Navrotsky, P.C. Burns, Stability of peroxide-containing uranyl minerals, *Science* 302 (2003) 1191–1193.
- [2] M. Amme, Contrary effects of the water radiolysis product H₂O₂ upon the dissolution of nuclear fuel in natural ground water and deionized water, *Radiation Environ. Biophys.* 90 (2002) 399–406.
- [3] G. Sattonnay, C. Ardois, C. Corbel, J.F. Lucchini, M.-F. Barthe, F. Garrido, D. Gosset, Alpha-radiolysis effects on UO₂ alteration in water, *J. Nucl. Mater.* 288 (2001) 11–19.
- [4] K. Walenta, On studtite and its composition, *Am. Mineral.* 59 (1974) 166–171.
- [5] R. Gupta, V.M. Pandey, S.R. Praneesh, A.B. Chakravarty, Study on an improved technique for precipitation of uranium from eluted solution, *Hydrometallurgy* 71 (2004) 429–434.
- [6] K.H. Gayer, L.C. Thompson, The solubility of uranium peroxide in acidic and basic media at 25 °C, *Can. J. Chem.* 35 (1958) 1649–1652.
- [7] T. Sato, Preparation of uranium peroxide hydrates, *J. Appl. Chem.* 1398 (1963) 361–365.
- [8] R. Djogic, V. Cuculic, M. Branica, Precipitation of uranium (IV) peroxide (UO₄) in sodium perchlorate solution, *Croat. Chim. Acta* 78 (4) (2005) 575–580.
- [9] R.C. Merritt, The Extractive Metallurgy of Uranium, Colorado School of Mines Research Institute, United States Atomic Energy Commission, 1971.
- [10] E.N. Pollock, U.S. Patent 4,701,310, Method and apparatus for producing uranyl peroxide from uranium and uranium alloy pieces (1985).
- [11] K.-W. Kim, D.-Y. Chung, H.-B. Yang, J.-K. Lim, E.-H. Lee, K.-C. Song, K. Song, A conceptual process study for recovery of uranium alone from spent nuclear fuel by using high-alkaline carbonate media, *Nucl. Technol.* 166 (2009) 170–179.
- [12] K. Imasaka, Y. Kato, J. Suehiro, Enhancement of microplasma-based water solubilization of single-walled carbon nanotubes using gas bubbling in water, *Nanotechnology* 18 (2007) 335602–335609.
- [13] F.W. Strelow, M.L. KoKot, T.N.V.D. Walt, B. Bhaga, Rationalized determination of uranium in rocks for geochemical prospecting using separation by ion exchange

- chromatography and spectrophotometry with arsenazo III, J. S. Afr. Chem. Inst. XXIX (1976) 97–104.
- [14] C.Y.-D. Tai, P.-C. Chen, W.-C. Chien, Particle nucleation and growth Encyclopedia of Surface and Colloid Science, vol. 1, no. 1, 2006, pp. 4452–4466.
- [15] G. Jarvinen, Precipitation and crystallization processes, Short course Introduction to Nuclear Chemistry and Fuel Cycle Separations, Vanderbilt University School of Engineering, Nashville, TN, December 16–18, 2008, CRESP (Consortium for Risk Evaluation with Stakeholder Participation), 2008.
- [16] K.A. Jackson, in: R.H. Doremus, B.W. Roberts, D. Turnbull (Eds.), Growth and Perfection of Crystals, Wiley, New York, 1958.
- [17] S. Finnie, R.I. Ristic, J.N. Sherwood, A.M. Zikic, Trans IChem E 74 (1996) 835.
- [18] K. Sangwal, Additive and Crystallization Processes from Fundamentals to Applications, John Wiley & Sons Ltd., West Sussex, England, 2007.