

Uranium(VI) Phosphate Precipitate Formation in a Carbonate Solution

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1. Introduction

Actinide ions including U(VI) form stable complexes with oxygen donating ligands. Various kinds of phosphorous compounds are used in a nuclear fuel cycle. Phosphate is an oxygen donating ligand and ubiquitous in nature. Thus, phosphate together with hydroxide and carbonate is one of the most important ligands controlling the chemical behavior of actinides in natural waters. U(VI) is immobilized in many phosphate minerals having the chemical forms of $M(I)UO_2PO_4 \cdot xH_2O$ [$M(I)=NH_4, Na$ or K , and $x=3-4$] or $M(II)(UO_2PO_4)_2 \cdot yH_2O$ [$M(II)=Mg, Ca, Ba, Cu, Fe$ or HAl , and $y=0-16$]. While, carbonate forms soluble species with U(VI) such as $UO_2(CO_3)_2^{2-}$, $UO_2(CO_3)_3^{4-}$ and $(UO_2)_3(CO_3)_6^{6-}$ [1]. U(VI) is associated with aqueous phosphate complexes at the pH range of 6 to 9 when the $[PO_4^{3-}]_T/[CO_3^{2-}]_T$ is greater than 0.1[2]. The study of the chemical behavior of U(VI) with the coexistence of phosphate and carbonate in alkaline pH ranges is highly desirable for the modeling of U(VI) in the environment.

2. Experiments

Ionic strength was adjusted with $NaClO_4$ to 0.1 M. Reactants were added into each test tube with a cap in the order of water, $NaClO_4$, Na_2HPO_4 , $NaOH$, $UO_2(ClO_4)_2$ and $NaHCO_3$ solutions. Total U(VI) concentration, $[UO_2^{2+}]_T$, was 3.33 mM. The value of $[PO_4^{3-}]_T/[UO_2^{2+}]_T$ and $[CO_3^{2-}]_T/[UO_2^{2+}]_T$ were 0.8 to 1.3, and 0 to 6, respectively. Carbonate free solutions were handled in a glove box of a nitrogen environment. Final pH range was 4 to 13. The solutions were shaken to equilibrate at 50 °C for 4 weeks, and at 20 °C for 4 weeks. Precipitates were separated by filtration(0.1 μm pore size) after centrifugations (Centrikon T-2060, Kontron, 15,000 rpm for 30 min). U and P were determined using ICP-AES (JY50P, Jobin Yvon). The spectra of the absorption and luminescence were measured with an UV/Visible spectrophotometer (Cary 3E, Varian) and fluorospectrophotometer (FL900CD, Edinburgh), respectively.

3. Results and discussion

The measured U(VI) solubility in the carbonate free solutions was much smaller than 0.01 mM. The mole ratio of the phosphate to U(VI) in the precipitate, $[PO_4^{3-}]_{ppt}/[UO_2^{2+}]_{ppt}$, at various pHs is presented in Figure 1. The ratio in the precipitate was exactly the same as the

total ratio at $pH < 8$ when the latter ratio was not more than 1.0. This suggests that U(VI) equivalent to phosphate formed the $NaUO_2PO_4 \cdot xH_2O$ precipitate and the excess of U(VI) formed the hydroxides precipitates. The $[PO_4^{3-}]_{ppt}/[UO_2^{2+}]_{ppt}$ is 1.0 even at $[PO_4^{3-}]_T/[UO_2^{2+}]_T = 1.3$, indicating that $NaUO_2PO_4$ is a major precipitate at $pH < 9$. The $[PO_4^{3-}]_{ppt}/[UO_2^{2+}]_{ppt}$ decreased to less than 0.2 at $pH \approx 12$, indicating that hydroxides rather than phosphates are the major species of the U(VI) precipitates in a high alkaline solution.

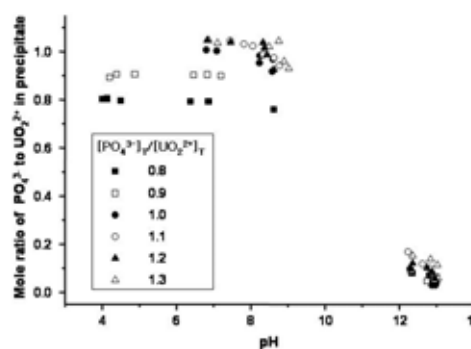


Figure 1. Mole ratio of phosphate to U(VI) in the precipitate formed in carbonate free solutions of various pHs.

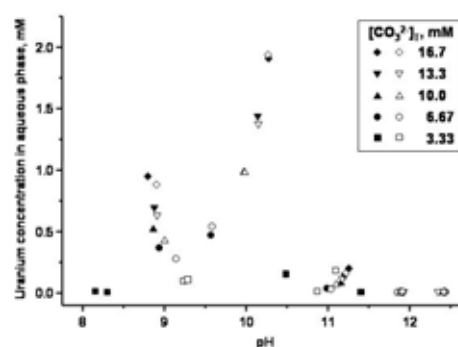


Figure 2. Change of U(VI) solubility against pH in the presence of carbonate at $[PO_4^{3-}]_T/[UO_2^{2+}]_T = 1.0$ (solid) and 1.2 (open).

The change of U(VI) solubility against the pH in the presence of carbonate at $[PO_4^{3-}]_T/[UO_2^{2+}]_T = 1.0$ and 1.2 is shown in Figure 2. The U(VI) solubility increased as the total carbonate concentration increased, and was slightly lower at $[PO_4^{3-}]_T/[UO_2^{2+}]_T = 1.0$ than at 1.2. The effect of the pH shows a similar trend for all the $[PO_4^{3-}]_T/[UO_2^{2+}]_T$ and $[CO_3^{2-}]_T/[UO_2^{2+}]_T$ systems. The solubility increased with the pH, decreased abruptly

around pH 10.5, and then approached zero at pH>11.5. This abrupt change at around pH 10.5 was also found in the phosphate concentration change.

The phosphate concentration in the aqueous phase at various pHs at $[\text{PO}_4^{3-}]_{\text{T}}/[\text{UO}_2^{2+}]_{\text{T}} = 1.0$ and 1.2 is shown in Figure 3. The concentration increased with the pH, decreased abruptly around pH 10.5, and then increased with the pH. These abrupt changes at around pH 10.5 suggest that the precipitate formation aspects below and above pH 10.5 are different from each other. It is explained by the competition of the phosphate precipitation with the soluble carbonate formation at pH<10.5 and with the hydroxide precipitation at pH>10.5 on comparing the relative concentration change of the dibasic carbonate, tribasic phosphate and hydroxide with an increasing pH.

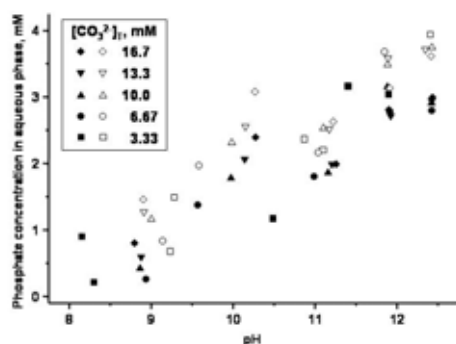


Figure 3. Change of phosphate concentration in aqueous phase against the pH in the presence of carbonate at $[\text{PO}_4^{3-}]_{\text{T}}/[\text{UO}_2^{2+}]_{\text{T}} = 1.0$ (solid) and 1.2(open).

The absorption spectra of some solutions showing high U(VI) concentrations are presented in Figure 4. The intensities are proportional to the U(VI) concentrations and the wavelengths of the absorption peaks coincide with those of the U(VI) carbonate complexes, suggesting that the dissolved U(VI) species are only carbonate complexes and no mixed complexes with phosphate are formed even in the presence of phosphate.

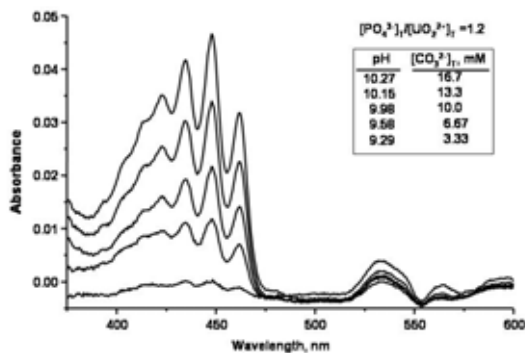


Figure 4. Absorption spectra of some solutions with high U(VI) concentrations at $[\text{PO}_4^{3-}]_{\text{T}}/[\text{UO}_2^{2+}]_{\text{T}} = 1.0$ (solid) and 1.2(open).

The change of $[\text{PO}_4^{3-}]_{\text{ppt}}/[\text{UO}_2^{2+}]_{\text{ppt}}$ against the pH in the presence of carbonate is presented in Figure 5. $[\text{PO}_4^{3-}]_{\text{ppt}}/[\text{UO}_2^{2+}]_{\text{ppt}}$ was nearly 1.0 below pH 9 though U(VI) was dissolved by the carbonate complexes formation, suggesting that only NaUO_2PO_4 precipitate existed and reacted with the carbonate at pH<9. The ratio decreased almost linearly with the pH even at pH>10.5 where soluble carbonate are not formed. This requires that other species without phosphate such as a carbonate and/or hydroxides should be produced together to form mixed precipitates. These were supported by the fluorescence spectra of the precipitates showing sharp and discrete peaks of single species at pH<9, while it was broad and shapeless peaks of the mixed species at pH>9.

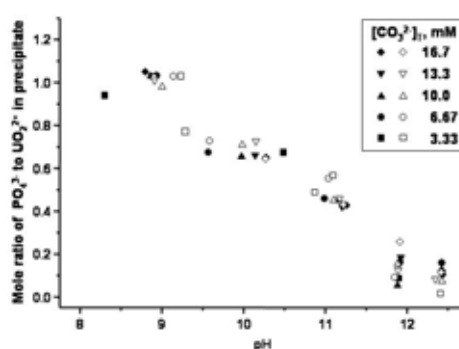


Figure 5. $[\text{PO}_4^{3-}]_{\text{ppt}}/[\text{UO}_2^{2+}]_{\text{ppt}}$ change against the pH in the presence of carbonate at $[\text{PO}_4^{3-}]_{\text{T}}/[\text{UO}_2^{2+}]_{\text{T}} = 1.0$ (solid) and 1.2(open).

4. Summary

The precipitation of U(VI) in the presence of phosphate and carbonate was investigated in the pH range of 4 to 13 and the following was obtained as a result of this experimental condition. U(VI) precipitates as a NaUO_2PO_4 at pH<9 but as mixtures of phosphate, hydroxides and/or carbonate at pH>9. The portion of the phosphate in the precipitate decreases almost linearly to near zero with an increasing pH in the range of 9 to 13. The U(VI) phosphate is dissolved by the carbonate complex formation at pH<10.5. The ternary complex of a carbonate and phosphate is not found.

REFERENCES

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- [2] A. Sandino, and J. Bruno, *Geochim. Cosmochim. Acta*, Vol.56, p. 4135, 1992.