

## Formation of U(IV) Nanoparticles and Their Growth Mechanism in Mildly Acidic Aqueous Phases

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### 1. Introduction

Under deep geological conditions reduced forms of radionuclides (RNs) occur owing to the anoxic environment and play dominant roles on immobilization or migration of radionuclides. Among these RNs tetravalent uranium (U(IV)) is a representative reduced species showing distinct chemical behaviors compared to those in oxidized states, e.g., hexavalent uranium (U(VI)). It is generally known that U(IV) exists mostly in solid forms in near neutral aqueous solutions, such as U(IV) hydrous oxide ( $\text{UO}_2 \cdot x\text{H}_2\text{O}(\text{am})$ ) and crystalline U(IV) ( $\text{UO}_2(\text{cr})$ ) precipitates due to its low solubility. Previous studies suggest that U(IV) nanoparticle (NP) formation is one of key steps in mineralization or immobilization of uranium which can be mediated either by microbes or by abiotic geochemical reactions [1].

Colloidal NPs in a groundwater system are potential carrier phases influencing RN migration in subsurface environment. However, the mechanism of U(IV) NP formation and the potential reaction intermediates during this solid phase formation process have not been elucidated in detail so far. In this study we attempted to examine the U(IV) nanoparticle formation reactions preceded by the hydrolysis of  $\text{U}^{4+}$  at different pHs, concentrations and temperatures. The kinetics of U(IV) NP formation from dissolved U(IV) species was monitored under mildly acidic conditions (pH 2~3) mainly by using UV-Vis absorption spectrophotometry. Dynamic light scattering (DLS) analysis, nanoparticle tracking analysis (NTA) and transmission electron microscopy (TEM) were used to characterize the NPs produced during the reactions.

The results demonstrate that the U(IV) NP formation process is very sensitive toward temperature variation. The main outcome of this study is the discovery of the autocatalytic nature of U(IV) NP formation from the supersaturated  $\text{U}(\text{OH})^{3+}$  solution in a mildly acidic aqueous solution. This implies that U(IV) NPs form through at least two main reaction steps. We propose that during this conversion process the intermediate species provide reactive or catalytic reaction sites likely at the terminal of the structure or the surface of primary NPs. Nucleation and growth mechanisms of NP formation to primary particles and their clusters are discussed.

### 2. Experimental

The acidified U(VI) stock solution (pH 0) was electrochemically reduced using Hg/Pt electrodes to prepare a stock solution of U(IV), as described in [2]. The sample solutions were prepared by diluting the U(IV) stock solution without adding aliquots of a base solution. All solutions were handled in an Ar-filled glove box.

Absorption spectra of the U(IV) solutions were measured using a dual-beam UV-Vis spectrophotometer (CARY 3E, Varian, Palo Alto, CA) and quartz cuvette cells of 1-cm or 1-mm optical pathlength (Hellma, Germany). All spectra were measured at a controlled temperature ( $\pm 0.1^\circ\text{C}$ ) using a Peltier-controlled 6-cell cuvette holder (qChanger6, Quantum Northwest, WA). To investigate the reaction kinetics the change in UV-Vis absorption of a sample solution was monitored over time by regularly collecting the spectra. The spectral baseline was corrected for a quantitative analysis of dissolved U(IV) species, i.e.,  $\text{U}(\text{OH})^{3+}$ .

The DLS and NTA (Zetasizer Nano and Nanosight LM10, respectively, Malvern Instrument, UK) techniques were employed to directly measure the size distribution, zeta potential and concentration of NPs in the sample solutions. The particle size, morphology and crystalline structures of dry U(IV) NPs were measured from TEM image analysis (JEM 2100-F, JEOL).

### 3. Results and Discussion

#### 3.1 Formation of U(IV) NP at Various Temperatures

The kinetics of U(IV) NP formation reaction in a solution containing dissolved U(IV) species was monitored in situ using a temperature-controlled cell block installed within a UV-Vis spectrophotometer.

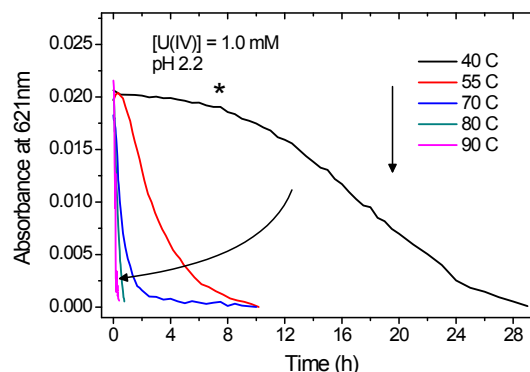


Fig. 1. Temperature dependence of U(IV) NP formation kinetics as indicated by consumption of  $\text{U}(\text{OH})^{3+}$ . The

decrease of the characteristic absorption band of  $U(OH)^{3+}$  at 621nm was monitored over time at different temperature ( $I = 0.1 \text{ M, NaClO}_4$ ).

Under a mildly acidic condition ( $\text{pH} > \sim 2$ ) the concentration of  $U^{4+}$  is very low and  $U(OH)^{3+}$  is the predominant dissolved U(IV) species. Formation of a solid phase,  $UO_2(\text{cr})$  is predicted based on the reported thermodynamic data of U(IV) solubility and hydrolysis [3]. However, we proved that  $UO_2(\text{cr})$  formation is kinetically hindered at room temperature or under lower temperature in a previous study [4]. It was demonstrated that at an elevated temperature U(IV) NP formation can be facilitated and spectrophotometrically analyzed by monitoring the consumption of  $U(OH)^{3+}$  in the solution. As similarly shown in Fig. 1, the NP formation becomes accelerated as the reaction temperature increases. TEM image analysis shows that the major solid phase produced throughout the reaction time is the a few-nm size  $UO_2(\text{cr})$ , i.e., primary  $UO_2$  NP (see Fig. 2), or its aggregate.

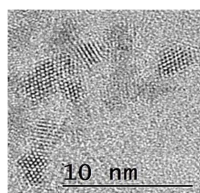
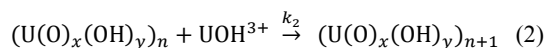
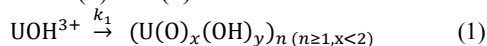


Fig. 2. TEM image of crystalline  $UO_2$  primary NP showing the periodic atomic arrangement having 1- or 2-dimensional orientation. The primary NP size is approximately 2-3 nm as prepared at elevated temperature (80-90 °C) in 5 h.

### 3.2 Kinetics and Mechanism of U(IV) NP

Interestingly, there is an initial lag phase of the reaction in an intermediate temperature range ( $< 50 \text{ }^\circ\text{C}$ ), as marked with a star symbol on the trace of the reaction at  $40 \text{ }^\circ\text{C}$  in Fig. 1. Such a slow reaction phase is reproducibly observed, but its kinetics is dependent on pH, concentration and temperature. Its sigmoidal reaction profile indicates the involvement of at least two reaction steps including an initially slow reaction (a rate-determining step (r.d.s.)) and a rapid one later. The reaction product of the initial r.d.s. is served as a more reactive or catalytic intermediate to facilitate the reaction at the later stage. Such a reaction is called 'autocatalytic reaction'. As a result of the reaction kinetic analysis we propose a two-step autocatalytic mechanism of U(IV) NP production reaction as shown in the reaction (1) and (2).



The reaction (1) is the r.d.s. responsible for the initial lag phase. The overall reaction rate ( $r$ ) can be expressed as follows:

$$r = -\frac{dc}{dt} = k_1c + k_2c(c_0 - c), c = [UOH^{3+}] \quad (3)$$

$$r/c = k_1 + k_2(c_0 - c) \quad (4)$$

where  $c_0$  is the initial  $U(OH)^{3+}$  concentration and  $c$  is the one spectrophotometrically measured at a given

time during the reaction. The equation (4) is obtained by rearranging the equation (3). Thus, the linear relationship between ' $r/c$ ' vs. ' $c$ ' is a proof of an autocatalytic reaction.

In fact, a reconstructed plot of the reaction data at  $40 \text{ }^\circ\text{C}$  in Fig. 1 using the equation (4) exhibits a linearity as shown in Fig. 3. This result clearly indicates the autocatalytic property of the reaction. Based on this kinetic analysis we conclude that the reaction intermediate has oxide linkages which require an activation energy to be formed from the reactant,  $UOH^{3+}$ , and result in irreversibility of the reaction. However, the zeta potential measured during the reaction has a positive value, approximately +30-40 mV. This indicates that the intermediates have uraninite-like  $UO_2(\text{cr})$  inner structures, but the surface or the terminal structure is positively charged likely with coordination of hydroxyl ligand, i.e.,  $(U(O)_x(OH)_y)_n \quad (x < 2)$ . It is thought that once this intermediate is formed it serves as a nuclear for NP growth providing sites for facilitating  $UO_2$  crystal growth and finally producing the primary NPs. Using DLS and NTA methods the overall sizes of the NP aggregates or clusters were measured to range from approximately 20 nm to 60 nm.

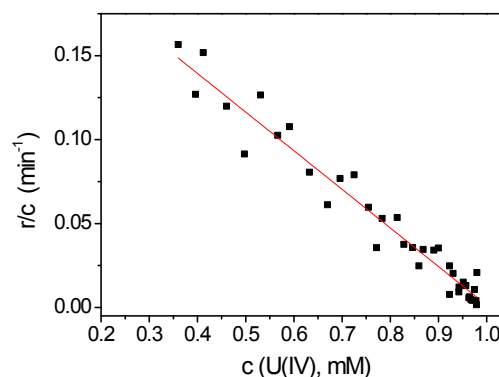


Fig. 3. Temperature dependence of U(IV) NP formation kinetics as indicated by consumption of  $U(OH)^{3+}$ . The decrease of the characteristic absorption band of  $U(OH)^{3+}$  at 621nm was monitored over time at different temperature ( $I = 0.1 \text{ M, NaClO}_4$ ).

## 4. Conclusions

The U(IV) NP formation process is investigated in mildly acidic aqueous solutions using UV-Vis spectrophotometry and various NP characterization methods. Susceptibility of the NP formation reaction toward temperature change is analyzed. Sigmoidal reaction kinetic in an intermediate temperature range ( $35\text{-}50 \text{ }^\circ\text{C}$ ) is interpreted as a result of autocatalysis involving multi-step reactions. The structure of reaction intermediates is proposed to contain oxide linkage. In the presentation the proposed mechanism of the U(IV) NP formation reaction and the properties of primary NPs and their clusters will be discussed in detail.

## ACKNOWLEDGEMENTS

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