PRECIPITATION AND ADSORPTION OF URANIUM(VI) UNDER VARIOUS AQUEOUS CONDITIONS

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Abstract : The uranium speciation at underground aqueous conditions was investigated by an equilibrium model calculation as well as precipitation experiments. Complexation reactions involving the aqueous and solid-phases of uranium hydroxide, uranium hydroxyl carbonate, uranium carbonate, and uranium oxide were considered in the model calculation using MINTEQA2 geochemical code. The batch-type precipitation or adsorption experiments were carried out at pHs 4-10 under 0% CO_2, air, and, 10% CO_2 conditions. The dominant uranium species is UO_2^{2+} at pHs 5 or below. Uranium is precipitated as species of β-$UO_2(OH)_2(s)$ at a neutral pH. The precipitated uranium increases rapidly and then decreases with the increment of pH. The aqueous phases having a negative charge such as $UO_2(OH)_3^-$, $(UO_2)_2CO_3(OH)_3^-$ and $UO_2(CO_3)_3^{4-}$ are dominant species at a high pH. Adsorption characteristics of uranium on kaolinite are explained by complexation reaction on mineral surface and precipitation of uranium. The adsorbed fraction and precipitated fraction have the same tendencies as a function of pH. However, the absolute amount of adsorbed uranium is higher than that of precipitated uranium. This difference is mainly caused by the surface complexation of UO_2^{2+} and other uranium species. The rapid decrease in the adsorbed amount at a high pH can also be caused by the uranium species having a negative charge.

INTRODUCTION

Industrial or radioactive waste has been disposed of at an underground repository. If the hazardous elements in the disposed waste are exposed to groundwater, they can dissolve into water. There is, therefore, a potential for these hazardous elements to migrate and easily enter the terrestrial and aquatic environments. The migration behavior in the geosphere greatly depends on the chemical property of the hazardous elements as well as their interaction with surrounding solids.[1,2] One of the important phenomena to limit the migration of the elements is their precipitation. Another process to retard the transport of the elements is their adsorption on underground matrices. Precipitation is occurred by solid-phase formation of the elements under the solubility limits in the groundwater. Precipitation and solubility limits determine the chemical species of the element in the aquatic systems. The chemical species of the elements has an important role in the evaluation of their adsorption behavior. In addition, the adsorption characteristics of the elements on surrounding solids are mainly

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affected by the surface property of the solids.[3,4]

Uranium is a widespread environmental contaminant resulting from mining and manufacturing activities related to nuclear power. Uranium has a large quantity of nuclear waste and is the most common radionuclide contaminant in groundwater and underground solids. Chemical properties of uranium are very complex and not clearly known at present.[5] Investigation of their chemical behaviors, therefore, is an essential research work in establishing the conditions that would ensure safe waste disposal. Chemical behaviors of uranium including precipitation and adsorption are greatly influenced by the conditions of natural aquatic systems. These conditions comprise a wide variation of chemical parameters, e.g. pH from 4 to 9, Eh from -200 mV to +600 mV, CO_2 partial pressures from 0.03% to 10% ($10^{-3.5}$ atm. to 10^{-1} atm.), and various ionic strength, etc.[6,7]

Underground matrices are mainly composed of rock-forming materials, together with a smaller amount of oxide and clay minerals. In spite of their smaller quantity, oxide and clay minerals have larger adsorption potential than rock-forming materials. For this reason, the studies on the adsorption of heavy metal and radionuclide with oxide and clay minerals have been identified as one of the important research works associated with waste disposal. Kaolinite is a typical clay mineral and it is composed of 1-1 type layered structure. If Si and Al in the layered structure change into Al and Mg by isomorphous substitution, the structure has negative charge and therefore cations become present between two layers. These cations in the interlayer of kaolinite can be substituted into other cations by ion-exchange reaction. At the crystalline edge of kaolinite, oxygen group and hydroxyl group are combined with Si and Al. Cations are also adsorbed onto those groups by surface complexation.[4,8~10]

Many studies have been conducted on the adsorption behavior of uranium with oxide and clay minerals because of its environmental significance.[11~13] Some research works up to date have been concerned with solid-phase formation of actinides.[14,15] This study investigated the speciation of uranium under various aquatic systems. The adsorption behavior of uranium under the aquatic system is investigated with particular placed emphasis on the distribution of its chemical species. Equilibrium distribution of aqueous and solid-phase uranium species was predicted by model calculation using geochemical code. Experimental investigation of the partitioning of aqueous and solid-phase uranium was also performed using precipitation method under different pH and CO_2 partial pressures. The adsorbed amount of uranium on kaolinite as a function of pH was investigated and then the adsorption behavior of uranium under various aqueous conditions was estimated.

METHODS

Modeling of Uranium Speciation

Equilibrium distribution of aqueous and solid-phase uranium at various pH and CO_2 conditions was calculated by the computer code MINTEQA2.[16] This code includes an extensive thermodynamic database and seven different algorithms for calculating adsorption. Precipitation-dissolution of metal and solid-phase saturation state can also be calculated by this geochemical model. The version 3.11 of MINTEQA2 contains 63 kinds of complexation reactions of U with ligands and the stability constants of each reaction. The U species, considered in these complexation reactions are UO_2^{2+} and U^{4+}. The ligands such as hydroxide, chloride, carbonate, fluoride, sulfate, phosphate, and silicate are included. In this study, 20 kinds of complexation reactions of U were added to the code to increase the reliability of the model calculations. The stability constants in the code were also updated. New complexation reactions and stability constants were referred by the studies of Grenthe, Neck and Bond.[5,17,18] In this model calculation, complexation reactions of UO_2^{2+} with hydroxide

Table 1. Reactions of aqueous and solid uranium species and stability constants used for equilibrium model calculation

Reactions	log K
Aqueous species	
$UO_2OH^+ \Leftrightarrow UO_2^{2+} + H_2O - H^+$	-5.70
$(UO_2)_2(OH)_2^{2+} \Leftrightarrow 2UO_2^{2+} + 2H_2O - 2H^+$	-5.70
$(UO_2)_3(OH)_5^+ \Leftrightarrow 3UO_2^{2+} + 5H_2O - 5H^+$	-15.79
$(UO_2)_3(OH)_4^{2+} \Leftrightarrow 3UO_2^{2+} + 4H_2O - 4H^+$	-11.90
$UO_2(OH)_2$ (aq) $\Leftrightarrow UO_2^{2+} + 2H_2O - 2H^+$	-12.10
$UO_2(OH)_3^- \Leftrightarrow UO_2^{2+} + 3H_2O - 3H^+$	-20.00
$UO_2(OH)_4^{2-} \Leftrightarrow UO_2^{2+} + 4H_2O - 4H^+$	-32.40
$(UO_2)_2(OH)^{3+} \Leftrightarrow 2UO_2^{2+} + H_2O - H^+$	-2.70
$(UO_2)_3(OH)_7^- \Leftrightarrow 3UO_2^{2+} + 7H_2O - 7H^+$	-31.49
$(UO_2)_4(OH)_7^+ \Leftrightarrow 4UO_2^{2+} + 7H_2O - 7H^+$	-21.90
$UO_2CO_3(aq) \Leftrightarrow UO_2^{2+} + CO_3^{2-}$	9.80
$UO_2(CO_3)_2^{2-} \Leftrightarrow UO_2^{2+} + 2CO_3^{2-}$	16.70
$UO_2(CO_3)_3^{4-} \Leftrightarrow UO_2^{2+} + 3CO_3^{2-}$	21.60
$(UO_2)_3(CO_3)_6^{6-} \Leftrightarrow 3UO_2^{2+} + 6CO_3^{2-}$	54.01
$(UO_2)_2CO_3(OH)_3^- \Leftrightarrow 2UO_2^{2+} + CO_3^{2-} + 3H_2O - 3H^+$	-0.86
$(UO_2)_3CO_3(OH)_3^+ \Leftrightarrow 3UO_2^{2+} + CO_3^{2-} + 3H_2O - 3H^+$	0.67
Solid species	
$UO_3(c) \Leftrightarrow UO_2^{2+} + H_2O - 2H^+$	-7.72
$UO_3(Gummite) \Leftrightarrow UO_2^{2+} + H_2O - 2H^+$	-10.41
$\beta\text{-}UO_2(OH)_2 \Leftrightarrow UO_2^{2+} + 2H_2O - 2H^+$	-4.94
$\beta\text{-}UO_2(OH)_2 \cdot H_2O(Schoepite) \Leftrightarrow UO_2^{2+} + 3H_2O - 2H^+$	-5.37
$UO_2CO_3(c,Rutherfordine) \Leftrightarrow UO_2^{2+} + CO_3^{2-}$	14.47

and carbonate ions were considered. The species of U^{4+} and the ligands such as chloride, sulfate, and phosphate were not included considering our experimental conditions. The complexation reactions and stability constants used in this calculation are summarized in Table 1. Uranyl hydroxide, uranyl hydroxyl carbonate, uranyl carbonate and poly uranyl compound as aqueous species are covered. The solid species such as uranyl oxide, uranyl hydroxide and uranyl carbonate are also included.

Precipitation Experiment

The stock solution of 1×10^{-2} M uranium was first prepared using $UO_2(NO_3)_2 \cdot 6H_2O$ (Merck Co. 99%). The 1×10^{-6} M UO_2^{2+} solution used for precipitation experiments was then made by diluting the stock solution. The $HClO_4$ and NaOH solutions of 0.1 M and 1 M concentrations were used for the pH adjust-

ment. $NaClO_4 \cdot H_2O$(Aldrich Co., 98%) was used for ionic strength adjustment. Batch-wise precipitation experiments were performed at a fixed temperature of 25°C under three different gaseous conditions. The gaseous conditions tested were nearly 0%, 0.03%, and 10% CO_2 partial pressure. Experiments under nearly 0% CO_2 partial pressure, which was performed to simulate CO_2-free condition, were carried out in the inert-gas glove box. The glove box was filled with N_2 gas with 99.999% purity. Almost CO_2-free conditions were verified by the analysis of GC (DID, HP Agilent). The CO_2 concentration in the glove box did not exceed 3.2 ppm. 0.03% and 10% CO_2 partial pressures were to simulate atmospheric air and excess CO_2 conditions, respectively. 10% CO_2 condition was maintained by continuously bubbling 10% CO_2 gas (99.999% purity with remainder consisting of N_2) through the UO_2^{2+} solution at a flow rate of about 10 ml/min. The

concentration of UO_2^{2+} in the solution was fixed at 1×10^{-6} M. The ionic strength of the solution was constant to the conditions of 0.01 M $NaClO_4$. To investigate the pH effect on precipitation, the pHs of solution were varied from 4 to 10. The precipitation time was 3 days. 5 mL of sample was taken from the solution at equilibrium, and the liquid and the precipitate were separated by using 0.45 μm membrane filter of cellulose acetate (Corning 21053-25). The concentration of U in the liquid was determined by using ICP-AES(ICPS-1000 III, Shimadzu) and ICP-MS(PQ3, VG Elemental). The concentration of U in the precipitate was calculated from the concentration difference in the solutions before and after precipitation. The pH of solutions before and after precipitation were measured by using combined glass electrode (Metrohm 6.0233. 100)

Adsorption Experiment

Batch-wise adsorption experiments were also carried out at a constant temperature of 25℃ under three different gaseous conditions. Three gaseous conditions correspond to nearly 0%, 0.03%, and 10% CO_2 partial pressures. The conditions of adsorption experiments are controlled by same methods as those of precipitation experiments. The concentration of UO_2^{2+} in the solution was fixed at 1×10^{-6} M. The

ionic strength of the solution was maintained constant 0.01 M $NaClO_4$. The pHs of solution were varied from 4 to 10. Kaolinite was added to the prepared UO_2^{2+} solution and the reaction solutions were then shaken during 3 days. The amount of kaolinite added to the 40 ml of UO_2^{2+} solution was 0.04 g. It corresponds to the solid to solution ratio of 1 g/L. The separation method of liquid and solid in the adsorption experiments is same as that in the precipitation experiments. The concentration of U in the liquid was determined by using ICP-AES and ICP-MS.

RESULTS AND DISCUSSION

Modeling of Uranium Speciation

Equilibrium distributions of uranium species under different CO_2 conditions by model calculation are shown in Figures 1, 2, and 3. Figure 1 is the calculated result of U speciation under 0% CO_2 condition. Uranium almost exists as UO_2^{2+} at pHs 5.5 or below. Uranium also exists as a form of UO_2OH^+ and $(UO_2)_3(OH)_5^+$ between pH 5 and 6.5. The maximum distribution of UO_2OH^+ and $(UO_2)_3(OH)_5^+$ are 19% and 36%, respectively. Uranium is precipitated as a form of β-$UO_2(OH)_2(s)$ between pH 6 and 9. The distribution percentage of the solid-phase is over 80%. The dominant solid-phase is uranyl hydroxide because of CO_2 free condition. Uranium exists as $UO_2(OH)_3^-$ at pHs 9 or above. The distribution of U species under the air condition is shown in Figure 2. Air condition corresponds to the condition of $10^{-3.5}$ atm. CO_2 partial pressure. Uranium exists as UO_2^{2+} at pHs 5.5 or below and as UO_2OH^+ and $(UO_2)_3(OH)_5^+$ between pH 5 and 6.5. The distribution below pH 6.5 is same as that in Figure 1. But uranium is precipitated as species of β-$UO_2(OH)_2(s)$ between 6 and 7.5. The maximum percentage of the solid-phase is 54%. This solid-phase disappears at pH 7.5 and U species including carbonate is formed above pH 7. The dominant species in the pH range of 7~9 and
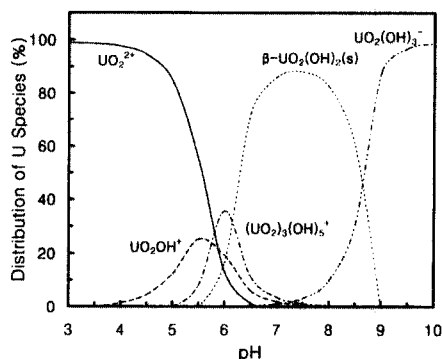

Figure 1. Calculated distribution of aqueous and solid uranium species in the 1×10^{-6} M solution equilibrated under 0% CO_2 condition.

Figure 2. Calculated distribution of aqueous and solid uranium species in the 1×10^{-6} M solution equilibrated under air condition.

Figure 3. Calculated distribution of aqueous and solid uranium species in the 1×10^{-6} M solution equilibrated under 10% CO_2 condition.
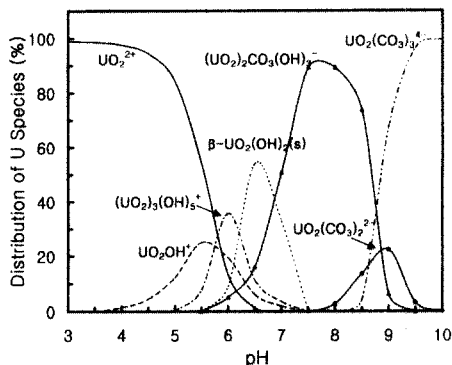
above 9 are $(UO_2)_2CO_3(OH)_3^-$ and $UO_2(CO_3)_3^{4-}$, respectively. The aqueous phases of uranyl ion, uranyl hydroxyl carbonate and uranyl carbonate are formed as the pHs of solution increase. The solid-phase is uranyl hydroxide around pH 7. Figure 3 shows the equilibrium distributions under saturated CO_2 conditions. Uranium exists as UO_2^{2+} at pHs 4.5 or below. Uranium species including carbonate start to be formed above pH 4. The dominant species in the pH range of $4.5 \sim 6$, $6 \sim 7.5$ and above 7 are the aqueous species of $UO_2CO_3(aq)$, $UO_2(CO_3)_2^{2-}$ and $UO_2(CO_3)_3^{4-}$, respectively. Solid-phase is not found in this calculation.

It is found from equilibrium model calculations that the dominant species at pHs 5.5 or below is uranyl ion although the CO_2 conditions were varied. Uranium is precipitated as a hydroxide form of β-$UO_2(OH)_2(s)$ at a neutral pH under 0% CO_2 and air conditions. The aqueous phase of uranium hydroxide, uranium hydroxyl carbonate and uranium carbonate are dominant species at a high pH. These species have an anionic charge.

Precipitation of Uranium

The results of precipitation experiments are shown in Figure 4. The amount of solid-phase uranium in the UO_2^{2+} solution under three different CO_2 conditions are represented with the pH of solution. As shown in Figure 4, the
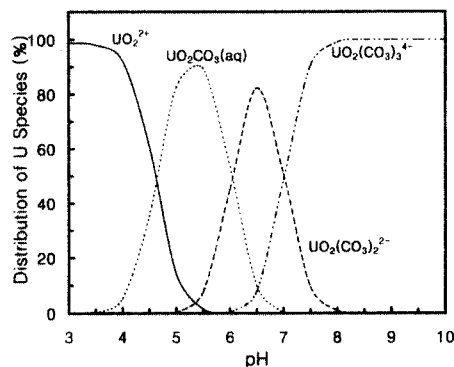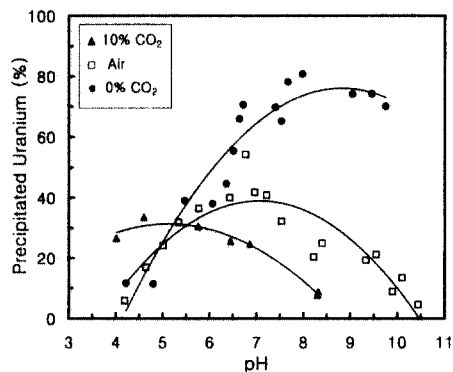

Figure 4. The amount of precipitated uranium as a function of pH in the 1×10^{-6} M solution equilibrated under 0%, air, 10% CO_2 conditions.

amounts of precipitated U under 0%, air, and 10% CO_2 conditions have different tendencies as a function of pH. In the case of 0% CO_2 condition, the precipitated amount of U was less than 30% of initial amount of U at pHs 5 or below. The amounts of solid U increased rapidly in the range of pH from 5 to 9. The precipitated U above 70% was maintained in the pH range of $7 \sim 10$. Then, the precipitated U began to decrease at pHs 9 or above. In the case of air condition, the precipitated U was less than 40% in the all pH range of $4 \sim 11$ except for 54% of precipitated U at pH 6.8. The amount of solid is relatively small in the low pH range. The amount of solid-phase

increased with the pH of solution and then decreased rapidly in the high pH range. The distribution of U precipitation under 10% CO_2 condition is different from that under 0% CO_2 or air condition. The precipitated U was about 30% of initial U at pHs 6 or below. The precipitated U decreased rapidly as the pH of solution increased. When the pH was above 8, the amount of solid-phase was less than 10%. This means that uranium under 10% CO_2 aqueous condition can not exist as a solid-phase in the high pH range.

Comparing these experimental results with the calculated distribution of U species in Figures 1, 2, and 3, the amounts of precipitated U agree with the line of solid-phase of β-$UO_2(OH)_2(s)$ in Figures 1 and 2. The precipitated U increases rapidly and then decreases with the increment of pH. The precipitated amounts are relatively small in the low and high pH range. There are maximum percentages in the pH range of 7~9 and 6.5~7 under 0% CO_2 and air conditions, respectively. The amount of precipitated U in the experiment of 10% CO_2 condition is different from that in the calculated distribution of U. To get exact information about precipitation behavior of uranium, the spectroscopic analysis of the aqueous and solid-phase should be additionally performed.

Adsorption of Uranium on Kaolinite

The adsorbed amounts of U as a function of pH under three different CO_2 conditions are shown in Figure 5. Under nearly 0% CO_2 condition, less than 40% of initial U was adsorbed below pH 5. The adsorbed amount of U increased rapidly as the pH increased. The adsorbed percentage reached more than 95% of initial U above pH 7 and then the amount was constant in the pH range from 7 to 9.5. But the adsorbed amount began to decrease above pH 9.5. When the CO_2 condition is air atmosphere, 28% of initial U was adsorbed at pH 4.4. The adsorbed amount increased sharply in the pH range of 4~7. The adsorbed percentage decreased slowly at pH 7 or above. Under 10%
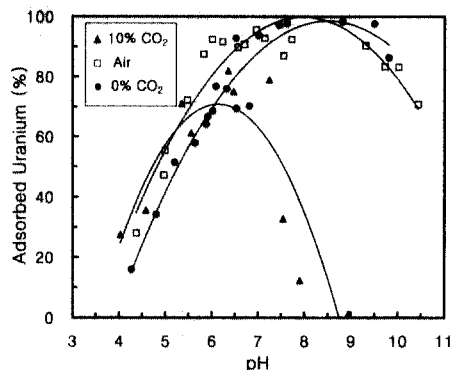

Figure 5. The amount of adsorbed uranium on kaolinite as a function of pH in the 1×10^{-6} M solution equilibrated under 0%, air, 10% CO_2 conditions.

CO_2 atmosphere, the adsorbed percentage of U increased with the increment of pH. At pH 6.4, the adsorbed amount reached 82% of initial U, which corresponds to the maximum adsorption. The adsorbed amount then decreased rapidly with the pH of solution. It was nearly 0% of initial U at pH 9.

Adsorption characteristics of metal on mineral can be explained by two parameters that influence metal behavior. One parameter is the chemical species of that metal and another is the surface property of mineral. The chemical species of metal varies as the pH of solution changes.[4,19] The equilibrium distribution of aqueous and solid-phase uranium species was first estimated by model calculation. The precipitation experiments were then performed to confirm the distribution of uranium species at various pH and CO_2 partial pressures. Uranium exists only as uranyl ion, UO_2^{2+}, at pHs 5 or below although the CO_2 conditions of solution varied. Uranium hydroxide of β-$UO_2(OH)_2(s)$ is precipitated in the pH range of 6~9. Uranium, hydroxide uranium hydroxyl carbonate and uranium carbonate having an anionic charge such as $UO_2(OH)_3^-$, $(UO_2)_2CO_3(OH)_3^-$, $UO_2(CO_3)_2^{2-}$ and $UO_2(CO_3)_3^{4-}$ exist in the high pH conditions. The 1-1 and 2-1 clay minerals such as kaolinite and montmorillonite, have a permanent charge between layers. Adsorption occurs at the ion-exchange sites of permanent

charge. However, alminol (AlOH) and silanol (SiOH) groups formed from the hydration of Al and Si contribute largely to the adsorption reaction. These functional groups are partly exposed to the edge of crystalline. The adsorption by functional groups, which is called surface complexation, greatly depends on the pH of solution, as the surface charge of functional group varies with the pH.[19,20] It is known that the progress of adsorption reaction at permanent charge site is different from that at edge site of SiOH and AlOH structure. Ion-exchange reaction is a main process at the site of mineral having the permanent charge. This process occurs at relatively low pH ranges. The adsorbed amount by ion-exchange is not varied with pH and it is affected by other cations.[21,22]

The adsorbed amounts in Figure 5 do not show these phenomena related to ion-exchange reaction. As shown in the results of Figure 5, the significant increase of adsorbed amount is found in the pH range of 4 ~ 7. This is resulted from the surface complexation between chemical species of U and hydroxyl groups of mineral surface. As the pH of the solution increases, functional groups at the edge of the kaolinite have negative charges and surface complexes are then formed by the reaction of anionic surface and uranium species. The dominant species of U in the pH range of 4 ~ 6 is UO_2^{2+} as shown in Figures 1 ~ 3. The uranyl cation has a good affinity with anionic surface. In the pH range of 6 ~ 9, the dominant species of U is solid-phase of β-$UO_2(OH)_2$(s). Therefore, the adsorbed amount is mainly contributed with the precipitated uranium. Comparing Figure 4 with Figure 5, the adsorbed fraction of U is higher than the precipitated fraction. This excess absorbed amount corresponds to the adsorbed amount by surface complexation of uranyl ion or other uranium species. At higher pH ranges, the adsorbed amount decreased rapidly. This explains that anionic species such as $UO_2(OH)_3^-$, $(UO_2)_2CO_3(OH)_3^-$, $UO_2(CO_3)_2^{2-}$ and $UO_2(CO_3)_3^{4-}$ exist in the higher

pH ranges and these species have not adsorption capacity with surfaces of mineral.

CONCLUSIONS

The distribution of uranium species under different underground disposal conditions was investigated by equilibrium model calculation as well as precipitation experiments. It is found from the results of equilibrium calculation that the dominant species is UO_2^{2+} at pHs 5 or below under different CO_2 conditions. Uranium is precipitated as species of β-$UO_2(OH)_2$(s) at a neutral pH under 0% CO_2 and air conditions. The aqueous phases having a negative charge such as $UO_2(OH)_3^-$, $(UO_2)_2CO_3(OH)_3^-$ and $UO_2(CO_3)_3^{4-}$ are dominant species at a high pH. From the precipitation experiments of 1×10^{-6} M UO_2^{2+} solution under 0% CO_2 and air conditions, the precipitated fraction of U agrees with the line of solid-phase of β-$UO_2(OH)_2$(s). The amounts of solid-phase are relatively small at low and high pHs. There are maximum percentages in the pH range of 6 ~ 8. The precipitated fraction of U in the experiment of 10% CO_2 condition is different from that in the calculated distribution of U. Adsorption characteristics of U on kaolinite can explained by complexation reaction on mineral surface and precipitation of uranium. The adsorbed amounts and precipitated amounts have the same tendencies as a function of pH. However, the absolute amount of adsorbed U is higher than that of precipitated U. The difference is mainly caused by surface complexation of UO_2^{2+} or other uranium species. The rapid decrease of adsorbed amount in the high pH range can be also caused by the anionic uranium species above mentioned. To confirm the chemical species of uranium, the aqueous and solid-phase of uranium are to be characterized additionally using analytical methods such as LIF and EXAFS spectroscopy. These methods are also very useful to explain the phenomena on the mineral surface.

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