Effects of pH on the Speciation of Radionuclides in Groundwater of Beishan Area, Gansu Province, China

Zhang Zhanshi*　Zhou Wenbin*　Fan Xianhua **

Speciation of radioactive nuclides is one of the most important factors in the study of migration and precipitation of the nuclides related to deep geological disposal of high level radwastes (HLW). Theoretical speciation analysis with thermodynamic equilibrium codes is an effective method. The authors have employed the EQ3NR, a computer program for geochemical aqueous speciation-solubility calculation, to evaluate the speciation of the key nuclides in the groundwater of Beishan Area, a potential area for hosting the HLW Repository of China. The calculated results showed that pH value as well as chemical composition of the water had a great impact on the speciation of key nuclides, such as Np, Pu, Am, U and Th, which would be released from HLW to the groundwater of Beishan Area. In addition, it was found that the speciation of nuclides varied from one to another. However, under alkaline conditions, the speciations were relatively simpler and hydroxyl complexes and carbonate complexes were dominant.

Key words: Geochemical modeling, Speciation, High level waste disposal, EQ3NR

1 INTRODUCTION

The national project on deep geological disposal (DGD) of HLW in China has been carried out for 15 years. After the national, regional and area screening, Beishan Area of Gansu Province in West China has been selected as a potential area for hosting the repository of HLW in China. Now, preliminary site characterization, including geological, hydrogeological, and geotechnical investigations, is on its way[1].

The speciation of radioactive nuclides in groundwater is one of the most important factors in the study of nuclide migration, which is a key factor in performance assessment of a repository. On the basis of hydrogeological and hydrogeochemical survey in Beishan area, the effects of pH on the speciation and solubility of several key radioactive nuclides are simulated by using EQ3NR.

2 CALCULATION CONDITIONS

Speciation and solubility calculation of nuclides were performed with the geochemical codes EQ3NR (Version 7.2a), a computer program for geochemical aqueous speciation-solubility calculation, developed by Wolery of Lawrence Livermore National Laboratory (LLNL). It is part of the EQ3/6 software package for geochemical modeling [2-3]. The attached thermodynamic data file is employed in this study. The numerical method employed is based on a hybrid Newton-Raphson technique, and the B-dot equation has been used for calculating activity coefficients. The nuclide concentrations adopted are 10^{-12}mol/L and the temperature adopted is 25℃. All the species of related nuclides in the attached data file are listed in Table 1. The emphasis is on the effects of pH on the speciation and solubility of nuclides in this study.

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3 CHEMICAL CHARACTERISTICS OF GROUND-WATER IN BEISHAN AREA

Beishan, a potential area for the HLW repository in Gansu Province of West China, is located in a typical arid climate region. As a part of the HLW DGD project of China, a preliminary characterization of hydrogeology and chemistry of the groundwater for the area has been carried out. The pH values for the shallow groundwater in this area are usually in the range of 7.1 to 8.8, temperature from 8 to 14℃, and the total dissolved solid (TDS) from 0.3 to 12g/L. The majority of shallow groundwater is of Cl-SO_4-Na and SO_4-Cl-Na type, followed by Cl-SO_4-Na-Ca type[4]. The water from Wuyi well, a 50-meter-deep well in Beishan area, is considered as the representative of the deep groundwater for the area. The chemical composition of the water, shown in Table 2, has been used in the modeling [4].

4 RESULTS AND DISCUSSIONS

4.1 Speciation of Radionuclides in Beishan Groundwater

Table 3 shows the speciations of the critical radionuclides in the groundwater of Beishan Wuyi well. The speciations of Am, Np and U, which are most hazardous radionuclides in HLW, are shown in Figs. 1 to 3.

Figure 1 indicates that in the water of Beishan Wuyi well, the dominant species of Am is $AmCO_3^+$ (84.42%) and the other species of Am are 10.15% of $Am(CO_3)_2^-$, 2.58% of $AmOH^{2+}$, 1.69% of $AmSO_4^+$and 0.941% of Am^{3+}.

From Fig.2, the dominant species of Pu is $PuO_2(CO_3)_2^{2-}$ (71.88%), and the others are PuO_2^+ (23.93%), PuO_2OH^+ (2.13%), $PuO_2F_3^-$ (0.802%) and PuO_2F_2(aq) (0.667%).

Figure 3 indicates that the dominant species of Np in the groundwater of Beishan Wuyi well is NpO_2^+(93.76%). The minor species are $NpO_2CO_3^-$(4.09%), NpO_2OH(aq) (1.84%).

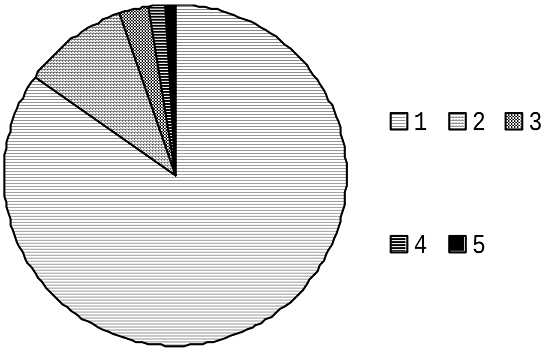
Table 1 The species of related nuclides in attached data file in EQ3NR [2,3]

Am^{3+}	AmF^{2+}	$AmO_2HCO_3(aq)$	$AmOH^{2+}$
$Am(H_2PO_4)_2^{+}$	AmF_2^{+}	$Am(CO_3)_3^{3-}$	$Am(OH)_2^{+}$
$Am(H_2PO_4)_3(aq)$	$AmF_3(aq)$	$AmCO_3^{+}$	$Am(OH)_3(aq)$
$Am(H_2PO_4)_4^{-}$	$AmCl^{2+}$	$Am(NO_3)_2^{+}$	$AmSO_4^{+}$
$AmH_2PO_4^{2+}$	$AmCl_2^{+}$	$AmNO_3^{2+}$	$Am(SO_4)_2^{-}$
NpO_2^{+}	NpF^{3+}	$(NpO_2)_3(OH)_5^{+}$	$NpO_2CO_3^{-}$
$Np(HPO_4)_4^{4-}$	NpF_2^{2+}	$(NpO_2)_2(OH)_2^{2+}$	$NpO_2(CO_3)_2^{2-}$
$Np(HPO_4)_5^{6-}$	$NpO_2F(aq)$	$Np(OH)_2^{2+}$	$NpO_2(CO_3)_3^{4-}$
$Np(H_2PO_4)_2^{+}$	$NpCl^{3+}$	$Np(OH)_3^{+}$	$NpO_2(CO_3)_2^{3-}$
$Np(H_2PO_4)_3(aq)$	$NpCl_2^{2+}$	$Np(OH)_4(aq)$	$Np(CO_3)_5^{6-}$
$Np(HPO_4)_2(aq)$	NpO_2Cl^{+}	$Np(OH)_5^{-}$	$NpSO_4^{2+}$
$NpO_2H_2PO_4(aq)$	$NpH_2PO_4^{2+}$	$NpO_2OH(aq)$	$NpO_2SO_4^{-}$
$NpO_2H_2PO_4^{+}$	$NpO_2HPO_4(aq)$	NpO_2OH^{+}	$Np(SO_4)_2(aq)$
NpO_2^{2+}	$NpO_2HPO_4^{-}$	$NpOH^{3+}$	$NpO_2SO_4(aq)$
PuO_2^{+}	PuO_2^{2+}		
PuO_2F^{+}	$PuO_2(CO_3)_2^{2-}$	$PuO_2SO_4(aq)$	$PuO_2OH(aq)$
PuF_2^{2+}	$PuH_2PO_4^{2+}$	$PuSO_4^{+}$	PuO_2OH^{+}
PuF_3^{+}	$PuHPO_4^{2+}$	$PuSO_4^{2+}$	$Pu(OH)_5^{-}$
$PuF_4(aq)$	$PuO_2H_2PO_4^{+}$	$Pu(SO_4)_2(aq)$	$Pu(OH)_2^{2+}$
PuF^{3+}	$Pu(HPO_4)_3^{2-}$	$Pu(SO_4)_2^{-}$	$Pu(OH)_3^{+}$
$PuO_2F_2(aq)$	$Pu(HPO_4)_4^{4-}$	$PuCl^{3+}$	$PuOH^{3+}$
$PuO_2F_3^{-}$	$PuO_2F_4^{2-}$	$Pu(OH)_4(aq)$	$PuOH^{2+}$
Th^{4+}	$Th(H_2PO_4)_2^{2+}$	$ThSO_4^{2+}$	$Th(OH)_2^{2+}$
ThF^{3+}	$Th(HPO_4)_2(aq)$	$Th(SO_4)_4^{4-}$	$Th(OH)_4(aq)$
ThF_2^{2+}	$Th(HPO_4)_3^{2-}$	$Th(SO_4)_2(aq)$	$Th_2(OH)_2^{6+}$
ThF_3^{+}	$ThH_2PO_4^{3+}$	$Th(SO_4)_3^{2-}$	$Th_4(OH)_8^{8+}$
$ThF_4(aq)$	$ThH_3PO_4^{4+}$	$ThCl_3^{+}$	$Th_6(OH)_{15}^{9+}$
$ThCl^{3+}$	$ThCl_4(aq)$	$ThCl_2^{2+}$	$ThOH^{3+}$
UO_2^{2+}	$U(CO_3)_4^{4-}$	UO_2OH^{+}	$UO_2(SCN)_2(aq)$
UF^{3+}	$U(CO_3)_5^{6-}$	UOH^{3+}	$UO_2(SCN)_3^{-}$
UF_2^{2+}	$UO_2(CO_3)_2^{2-}$	$U(OH)_4(aq)$	UO_2SCN^{+}
UF_{3+}	$UO_2(CO_3)_3^{-}$	$UO_2(OH)_2(aq)$	$U(SCN)_2^{2+}$
$UF_4(aq)$	$UO_2(CO_3)_3^{4-}$	$UO_2(OH)_3^{-}$	$USCN^{3+}$
UF_5^{-}	$UO_2CO_3(aq)$	$UO_2(OH)_4^{2-}$	$UO_2(N_3)_2(aq)$
UF_6^{2-}	$UO_2(H_2PO_4)(H_3PO_4)^{+}$	$UO_2(SO_3)_2^{2-}$	$UO_2(N_3)_3^{-}$
UO_2F^{+}	$UO_2(H_2PO_4)(H_3PO_4)^{+}$	$UO_2(SO_4)_2^{2-}$	$UO_2(N_3)_4^{2-}$
$UO_2F_2(aq)$	$UO_2(H_2PO_4)_2(aq)$	$UO_2IO_3^{+}$	UNO_3^{3+}
$UO_2F_3^{-}$	$UO_2H_2PO_4^{+}$	$UO_2(IO_3)_2(aq)$	$U(NO_3)_2^{2+}$
$UO_2F_4^{2-}$	$UO_2H_3PO_4^{2+}$	UI^{3+}	$UO_2N_3^{+}$
UO_2Cl^{+}	$UO_2HPO_4(aq)$	$UO_2S_2O_3(aq)$	$UO_2NO_3^{+}$
$UO_2Cl_2(aq)$	$UO_2PO_4^{-}$	$UO_2SO_3(aq)$	UBr^{3+}
$UO_2ClO_3^{+}$		$UO_2SO_4(aq)$	UO_2Br^{+}
UCl^{3+}		$U(SO_4)_2(aq)$	$UO_2BrO_3^{+}$

Table 2 Chemical composition of water from Wuyi well in Beishan Area[4]

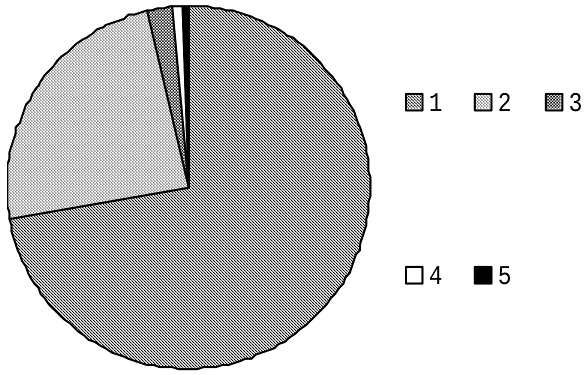
Element	Concentration	Element	Concentration	Element	Concentration	Element	Concentration
Na^{+}	47.83	NH_4^{+}	0.12	HCO_3^{-}	103.7	SiO_2（aq）	12.91
Ca^{2+}	73.88	Al^{3+}	0.06	Cl^{-}	61.35	NO_3^{-}	10.42
K^{+}	8.88	Mn^{2+}	0.022	F^{-}	0.26	Eh（V）	0.345
Mg^{2+}	8.98	Li^{+}	0.0112	Br^{-}	0.0001	pH	7.24
Cu	0.0001	Sr^{2+}	0.715	SO_4^{2-}	161.8		

Note: Measured at the 50m deep in-situ condition, mg/L



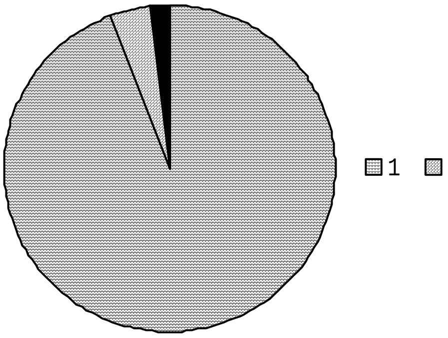
1: $AmCO_3^+$ 2: $Am(CO_3)_2^-$ 3: $AmOH^{2+}$
4: $AmSO_4^+$ 5: Am^{3+}

Fig.1 Speciation of Am in the groundwater



1: $PuO_2(CO_3)_2^{2-}$ 2: PuO_2^+ 3: PuO_2OH^+
4: Pu $O_2F_3^-$ 5: PuO_2F_2(aq)

Fig.2 Speciation of Pu in the groundwater



1: NpO_2^+ 2: $NpO_2CO_3^-$ 3: NpO_2OH(aq)

Fig.3 Speciation of Np in the groundwater

4.2 Solubility of nuclides under in-situ condition

Saturation indices(SI's) are important because they are measures of the thermodynamic driving forces behind the progress of reaction. These quantities form an important bridge between calculations that are purely thermodynamic and those that pertain to dynamic evolution. The saturation index (SI) is defined as :SI=log Q/K, where Q is the activity product and K the equilibrium constant for a dissolution reaction [2,3]. Following the above definition, saturation indices are zero for the case of exact saturation, negative for undersaturation, and positive for supersaturation. So the SI of a mineral could be used to discuss relative solubility of the nuclides in solution even though the concentration of actinides is assumed to be 10^{-12} mol/L. The higher the SI of a mineral is, the lower the solubility is.

Table 4 shows all the SI values of minerals containing the nuclides in decreasing order. The SI values of PuO_2, Thorianite and NpO_2 are higher than zero in Beishan Wuyi well. Those minerals would be precipitated and should not dissolve over 10^{-12} mol/L at that condition. Other minerals such as $AmOHCO_3$ are hardly formed and the solubility will be higher than 10^{-12} mol/L.

4.3 Effects of pH on the speciation of nuclide

The speciation of nuclides is greatly affected by the pH value. In this study a great emphasis is put on the effects of pH on the speciation and solubility of nuclides.

4.3.1 Speciation of Np as a function of pH

In the water of Beishan Wuyi well, the dominant species of Np is NpO_2^+（93.76%）and the minor speciations are $NpO_2CO_3^-$ and NpO_2OH(aq). The speciation of Np greatly varies with pH. In strong acid conditions, the dominant is $NpO_2^+$and the minor ones are NpO_2^{2+} and NpO_2SO_4(aq); in neutral conditions, the dominant is also NpO_2^+, but the coexisting ones are $NpO_2CO_3^-$ and NpO_2OH(aq); in weak alkaline to strong alkaline conditions, the dominant species change from $NpO_2CO_3^-$ to NpO_2OH(aq), and the minor ones are Np（CO_3）$_3^{4-}$ and NpO_2（CO_3）$_2^{3-}$. Figure 4 gives the detailed evolution.

4.3.2 Speciation of Pu as a function of pH

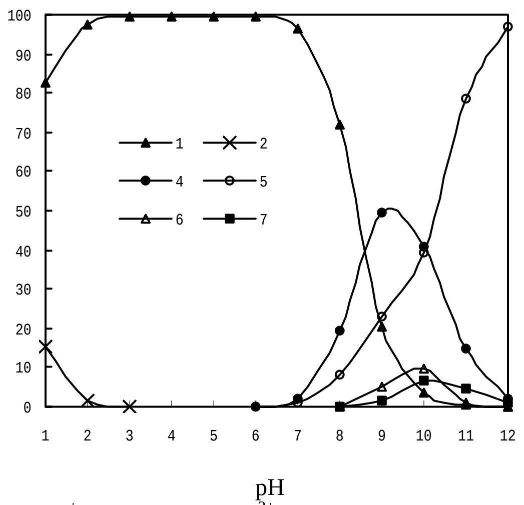
The calculated species of Pu were $PuO_2(CO_3)_2^{2-}$, PuO_2^+, PuO_2OH^+, $PuO_2F_3^-$ and PuO_2F_2(aq). The speciation of Pu also varies with pH. The dominant is PuO_2^{2+} and the minor ones are PuO_2SO_4 (aq) and PuO_2F^+ in strong acid conditions.

Table 3 Speciations of nuclides at pH 7.24

Speciation	Content(%)	Speciation	Content(%)	Speciation	Content(%)	Speciation	Content(%)
$AmCO_3^+$	84.42	$PuO_2(CO_3)_2^{2-}$	71.88	$UO_2(CO_3)_2^{2-}$	76.75	NpO_2^+	93.76
$Am(CO_3)_2^-$	10.15	PuO_2^+	23.93	$UO_2(CO_3)_3^{4-}$	12.82	$NpO_2CO_3^-$	4.09
$AmOH^{2+}$	2.58	PuO_2OH^+	2.13	$UO_2(OH)_2$(aq)	7.55	NpO_2OH(aq)	1.84
$AmSO_4^+$	1.69	$PuO_2F_3^-$	0.802	UO_2CO_3(aq)	2.64		
Am^{3+}	0.941	PuO_2F_2(aq)	0.667			$Th(OH)_4$aq	100

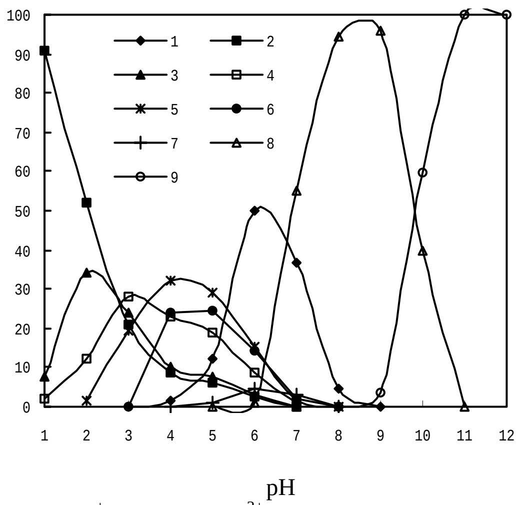
Table 4 Saturation indices of some minerals under in-situ condition

Minerals	SI	Minerals	SI	Minerals	SI
PuO_2	3.056	UO_2SO_4	-22.260	UCl_4	-82.060
Thorianite	2.038	$Pu(OH)_3$	-22.837	UCl_3	-85.468
NpO_2	0.801	UOFOH	-23.121	$UOBr_3$	-86.516
$AmOHCO_3$	-4.535	$UO_{2.3333}$(beta)	-23.313	$UBrCl_3$	-89.749
$Pu(OH)_4$	-5.067	UO_2Cl	-23.925	$UBrCl_2$	-93.106
$Th(OH)_4$	-5.755	UOF_2	-26.053	UF_6	-93.144
$Np(OH)_4$	-7.813	PuF_3	-26.654	$ThBr_4$	-94.923
$Am(OH)_3$	-8.088	UO_2SO_3	-34.078	$UO_2(NO_3)_2$	-95.388
UO_2CO_3	-8.788	$U(OH)_2SO_4$	-34.313	U_2F_9	-98.153
NpO_2OH(am)	-9.074	UF_4	-39.303	UBr_2Cl_2	-98.580
$Am(OH)_3$(am)	-9.588	PuF_4	-39.705	UCl_5	-101.941
UO_3(gamma)	-10.512	$U(SO_4)_2$	-43.353	UBr_2Cl	-102.520
$Th(SO_4)_2$	-10.776	$UOCl_2$	-45.446	$U_3O_5F_8$	-102.885
UO_3(beta)	-11.115	$U(CO_3)_2$	-47.637	$U_2O_2Cl_5$	-103.799
UO_3(alpha)	-11.444	$UClF_3$	-48.886	UBr_3Cl	-107.619
$UO_{2.25}$	-12.326	Pu_2O_3(beta)	-48.907	UBr_3	-111.104
ThF_4:2.5H_2O	-12.849	UO_2Br_2	-51.687	UBr_4	-115.931
UO_2FOH	-13.115	UOF_4	-55.985	UCl_6	-120.674
ThF_4	-14.711	$UOCl_3$	-57.170	UBr_5	-136.954
Uraninite	-15.060	UF_3	-59.364	$Th(NO_3)_4$:5H_2O	-159.130
PuO_2OH(am)	-15.263	ThC_{l4}	-60.135	U_4F_{17}	-175.896
$PuO_2(OH)_2$	-16.589	$UOBr_2$	-60.241	ThS_2	-183.636
$NpO_2(OH)_2$	-18.634	UCl_2F_2	-60.785	U_2C_3	-289.920
$UO_{2.6667}$	-18.666	UOCl	-62.756	Th_2S_3	-335.694
Uranophane	-18.709	$U_5O_{12}Cl$	-63.234	U_2S_3	-356.296
Np_2O_5	-19.176	UCl_3F	-72.509	U_3S_5	-387.750
UO_2F_2	-19.878	$U_2O_3F_6$	-76.014	Th_7S_{12}	-1203.551
UO_2(am)	-20.007	$U(SO_3)_2$	-77.655		



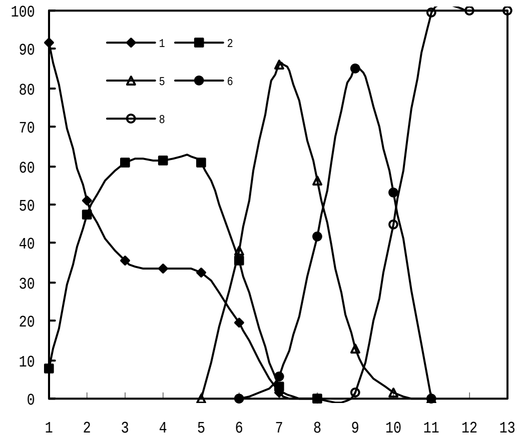
1: NpO_2^+　2: NpO_2^{2+};　3: NpO_2SO_4(aq);
4: $NpO_2CO_3^-$;　5: NpO_2OH(aq);
6: $NpO_2(CO_3)_3^{4-}$;　7: $NpO_2(CO_3)_2^{3-}$;

Fig.4 Speciation of Np as a function of pH



1: PuO_2^+;　2: PuO_2^{2+};　3: PuO_2SO_4(aq);
4: PuO_2F^+;　5: PuO_2F_2(aq);　6: $PuO_2F_3^-$;
7: PuO_2OH^+;　8: $PuO_2(CO_3)_2^{2-}$;　9: $Pu(OH)_5^-$;

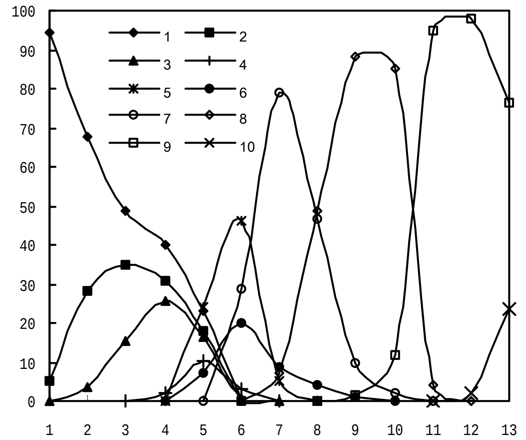
Fig . 5 Speciation of Pu as a function of pH



pH

1: Am^{3+}; 2: $AmSO_4^+$; 3: $Am(SO_4)_2^-$
4: AmF_2^+; 5: $AmCO_3^+$; 6: $Am(CO_3)^-_2$;
7: $AmOH_2^+$; 8: $Am(OH)_3(aq)$

Fig . 6 Speciations of Am as a function of pH



pH

1: UO_2^{2+}; 2: $UO_2SO_4(aq)$; 3:UO_2F; 4:UO_2OH;
5:$UO_2(CO_3)aq$; 6:$UO_2(OH)_2aq$; 7:$UO_2(CO_3)_2^{2-}$;
8:$UO_2(CO_3)_3^{4-}$; 9:$UO_2(OH)_3^-$; 10: $UO_2(OH)_4^{2-}$

Fig . 7 Speciations of U as a function of pH

In neutral conditions, the dominant is $PuO_2(CO_3)_2^{2-}$, but the coexisting ones are PuO_2^+, PuO_2OH^+, $PuO_2F_3^-$ and $PuO_2F_2(aq)$.

In weak alkaline to strong alkaline conditions, the dominant species change from $PuO_2(CO_3)_2^{2-}$ to $Pu(OH)_5^-$. Figuer 5 gives the detailed evolution.

4.3.3 Speciation of Am as a function of pH

In the water of Beishan Wuyi well, the calculated species of Am were $AmCO_3^+$, $Am(CO_3)_2^-$, $AmOH^{2+}$, $AmSO_4^+$and Am^{3+}. In strong acid conditions, the dominant species is Am^{3+}; in weak acid conditions, the dominant one is $AmSO_4^+$; in neutral conditions, the dominant one is $AmCO_3^+$; in weak alkaline the dominant one is $Am(CO_3)_2^-$; in strong alkaline the dominant one is $Am(OH)_3(aq)$. Figure 6 gives the detailed evolution.

4.3.4 Speciation of U as a function of pH

In the groundwater, the calculated U species were $UO_2(CO_3)_2^{2-}$, $UO_2(CO_3)_3^{4-}$, $UO_2(OH)_2(aq)$ and $UO_2CO_3(aq)$. When the pH changes from low to high, the dominant species of U is changed from UO_2^{2+} to $UO_2CO_3(aq)$, $UO_2(CO_3)_2^{2-}$, $UO_2(CO_3)_3^{4-}$, and finally to $UO_2(OH)_3^-$. The detailed evolution is given in Fig .7.

4.3.5 Speciation of Th as a function of pH

The speciation of Th differs from the above nuclides. Th $(OH)_4(aq)$ is the dominant species of Th when the pH is higher than 6. However in acid conditions, it changes with the pH, and the dominant species changes from $ThSO_4^{2+}$ to Th $(SO_4)_2(aq)$, then ThF_2^{2+}, and finally to $Th(OH)_4(aq)$ with increasing pH.

The speciation pattern of Th is different from other Actinides for the lack of thermodynamic data on Th carbonates as shown in Table1. Figure 8 shows the detailed evolution.

5. CONCLUSIONS

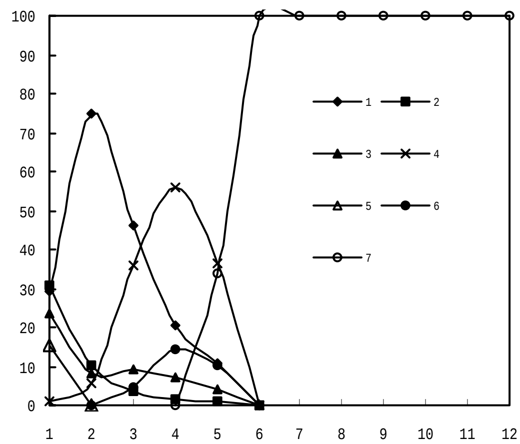
The following conclusions can be derived from the calculation:

The speciations of Np, Pu, Am, U and Th are affected not only by the chemical composition of the water but also by the pH value even with the same chemical composition.

Each of the five nuclides has its own speciation pattern, but the speciation of Pu, Am, U and Th is very complicated in acid conditions.

The speciation of nuclides is simpler in alkaline conditions, and the dominant species are hydroxyl complexes and carbonate complexes. It is thus important to study the adsorption and migration behavior of these species in geological materials.

The SI values of PuO_2, Thorianite and NpO_2 are higher than zero in Beishan Wuyi well. Those minerals would be precipitated and should not dissolve over 10^{-12} mol/L at that condition. Other minerals such as $AmOHCO_3$ are hardly formed and the solubility will be higher than 10^{-12} mol/L.



pH

1: $Th(SO_4)_2aq$; 2: $ThSO_4^{2+}$; 3: ThF_3^+
4: ThF_2^{2+}; 5: Th^{4+}; 6: ThF^{3+} 7:$Th(OH)_4aq$

Fig.8 Speciations of Th as a function of pH

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