74

JAERI-Research
99-047

原研

ANALYSIS OF AMERICIUM,
PLUTONIUM AND TECHNETIUM SOLUBILITY IN GROUNDWATER

August 1999

Seiji TAKEDA

日 本 原 子 力 研 究 所
Japan Atomic Energy Research Institute

Analysis of Americium, Plutonium and Technetium Solubility in Groundwater

Seiji TAKEDA

Department of Fuel Cycle Safety Research
Nuclear Safety Research Center
Tokai Research Establishment
Japan Atomic Energy Research Institute
Tokai-mura, Naka-gun, Ibaraki-ken

Safety assessments for geologic disposal of radioactive waste generally use solubilities of radioactive elements as the parameter restricting the dissolution of the elements from a waste matrix. This study evaluated americium, plutonium and technetium solubilities under a variety of geochemical conditions using the geochemical model EQ3/6. Thermodynamic data of elements used in the analysis were provided in the JAERI-data base. Chemical properties of both natural groundwater and interstitial water in buffer materials (bentonite and concrete) were investigated to determine the variations in Eh, pH and ligand concentrations (CO_3^{2-}, F^-, PO_4^{3-}, SO_4^{2-}, NO_3^- and NH_4^+). These properties can play an important role in the complexation of radioactive elements. Effect of the groundwater chemical properties on the solubility and formation of chemical species for americium, plutonium and technetium was predicted based on the solubility analyses under a variety of geochemical conditions. The solubility and speciation of the radioactive elements were estimated, taking into account the possible range of chemical compositions determined from the groundwater investigation.

i

地下水中におけるAm、Pu、Tcの溶解度の解析

日本原子力研究所東海研究所安全性試験研究センター燃料サイクル安全工学部
武田　聖司

　　放射性廃棄物の地層処分に対する安全評価において、放射性元素の溶解度はその廃棄体からの溶解を制限するためのパラメータとして用いられている。本研究では、処分場で予想される地下水組成の変化に対するAm、Pu、Tcの溶解度を、地球化学モデルEQ3/6を用いて算定した。現在原研で元素の熱力学データのデータベース化が行われており、そのデータベースを解析に使用した。また、Eh-pH条件と放射性元素との錯形成に関与する配位子（CO_3^{2-}、F^-、PO_4^{3-}、SO_4^{2-}、NO_3^-、NH_4^+）の濃度の変化を把握するため、緩衝材（ベントナイト及びセメント）中における間隙水及び地下水の組成データを調査した。地下水組成の変化に対する溶解度解析から、組成条件の変化がAm、Pu、Tcの溶解度及び化学種の生成に及ぼす影響を予測した。また、地下水組成の調査より推定された現実的な組成の変動範囲を考慮し、Am、Pu、Tcの溶解度と化学形を推定した。

Contents

目　　次

1. Introduction

In the safety assessment for geologic disposal of radioactive waste, the solubility of radioactive elements has been generally used as the parameter restricting the dissolution of the elements from a waste matrix. To provide data with safety assessment, the solubility has been experimentally measured for various chemical compounds of the elements of interest. The thermodynamic data have also been reported for possible aqueous species and solid phases formed in a solution. In parallel with these experimental works, solubilities of the elements under specific geochemical conditions in a disposal system have been evaluated with geochemical models such as PHREEQE[1] and EQ 3/6 [2] using thermodynamic data. Thus SKB[3], SKI[4] and YJT[5] have indicated the solubility and speciation calculated for some typical groundwaters under reducing and oxidizing conditions. In the reports of PNC[6] and PSI[7][8], the chemical property of groundwater characterized by chemical interaction with buffer materials and natural groundwater was predicted with the geochemical models, and the solubility and the dominant species were calculated under the predicted property. These analyses are based on the assumption that the geochemical interactions between these materials and groundwater are approximately described by the thermodynamic equilibrium modelling. This is because, considering that the groundwater velocity in buffer materials is extremely low, the time scale for these chemical interactions is supposed to be long enough to be equilibrated.

Geochemical model performance depends on the quality of thermodynamic data. The data base supporting the geochemical code should consist of reliable thermodynamic data for chemical species, of which the existence is experimentally identified in a groundwater system. The thermodynamic data for americium, uranium and technetium were reviewed and provided in the data base by Yamaguchi, T. and Takeda, S (1999)[9]. This data base also includes temporary thermodynamic data for other elements, which are referred from some existing data bases. Using this thermodynamic data base, referred to here as the Japan Atomic Energy Research Institute (JAERI) data base, the solubility and speciation of americium, plutonium and technetium in a reducing groundwater are estimated using the geochemical model, EQ3/6.

Solubility and speciation depend on the chemical properties of groundwater, such as pH, redox-potential (Eh), concentrations of dissolved elements and solid phase. Chemical characteristics of geologic disposal system are controlled by chemical reactions between groundwater and buffer materials. PNC[6] assumed that the buffer material in high level radioactive waste repository is a bentonite and predicted four typical chemical properties, fresh water (high pH and low pH) and saline water (high pH and low pH), to calculate the solubility limits of radioactive elements. In Japan, no decision has been made on the geologic setting, disposal repository site, inventory of radionuclides, type of buffer materials for radioactive waste from the fuel reprocessing cycle and research activities. This study focuseson the effect of variations in chemical properties such as Eh-pH condition and concentrations of several important ligands,.

CO_3^{2-}, F^-, PO_4^{3-} SO_4^{2-}, NO_3^- and NH_4^+, on solubility. The chemical properties of groundwater and interstitial water in buffer materials are determined from groundwater survey. The survey of natural groundwater was intended for the chemical properties measured in Japan and Sweden. Buffer materials were assumed to be bentonite or concrete. The survey for interstitial water in bentonite or concrete was based on measurements, experiments and model prediction. Solubility and speciation analysis for americium, plutonium and technetium were carried out under the various chemical conditions. The possible range of Eh-pH value and ligand concentrations is estimated from the groundwater survey. The objectives of this study are;

— to provide realistic solubility estimate in a reducing groundwater,
— to understand the effect of Eh-pH condition and ligand concentrations (carbon, phosphate, fluoride, sulphur and nitrogen on solubility and speciation, and
— to estimate conservative solubility, taking account of the possible range of Eh-pH value and ligand concentrations.

2. Geochemical Characteristic of Groundwater

2. 1 Investigation of chemical property

Wikberg, P.(1987)[10] classified the chemical property of the groundwater measured in the granitic rock in Sweden into four types of groundwater as shown in Table 2.1. Considering the discussion above and the results investigated by Wikberg, P., the chemical composition of groundwater is characterized by the concentration of specific cationic and anionic forms, Na^+, Ca^{2+}, HCO_3^-, Cl^- and SO_4^{2-}. It is of importance to grasp the variation of the concentration for their dissolved elements so as to discuss quantitative geochemistry of radioactive elements. It is considered that the concentration of some ligands has an influence on the solubility and speciation of radioactive elements. For example, the formation of carbonate complexes for radioactive elements is dependent on carbon concentration in a solution and may change its solubility. The chemical properties of both the measured natural groundwater and the interstitial water in the buffer materials (bentonite and concrete) were investigated to determine the possible range of Eh, pH and ligand concentrations.

2. 1. 1 Chemical property in natural groundwater

Chemical property of groundwater used in the study is from granitic rock in Sweden and sedimentary rock in Japan. TheSwedish data on the chemical properties for granitic rocks were used as there is not much information on chemical property for a granite in Japan and Eh data is comparatively abundant in Sweden. Twenty three samples in Sweden were collected[11][12]. The

Table 2.1 Classification of the chemical composition measured in the granitic rock of Sweden, according to Wikberg, P.(1987)[10].

Type A	Na-HCO3 type	Type A has the chemical composition of a typical granitic water. Calcite are dissolved. The concentration of Na^+ is high because of the cation exchange. The pH value ranges from neutraity to weak alkalinity.
Type B	Na-Cl · HCO3 type	Type B is the groundwater isolated in discontinuous fracture found in a rock for long time periods. The high concentration of Na^+ and Cl^- is caused by weathering of minerals. The pH value of Type B is a litte higher than that of Type A.
Type C	Na · Ca-Cl type	Type C is isolated in a rock for long-term periods and has the high pH influenced by the interaction with minerals. The high pH and Ca^{2+} concentration have resulted in precipitation of calcite and hence a decrease in the HCO_3^- concentration.
Type D	Na · Ca-Cl · SO4 type	Type D is the groundwater of a marine origin at neutral pH. The difference between Type C and D is especially characterized by SO_4^{2-} concentration and pH.

depth of sampling ranges from 70 to 860m. These data were divided between the fresh and saline water. The data of the fresh water are represented by $Na-HCO_3$ type and Na-Cl · HCO_3 type while those of the saline water belong to Na · Ca-Cl type and Na · Ca-Cl · SO_4 type as shown in Table 2.1. Table 2.2 shows the average values and the range of the chemical properties measured in the granitic rock in Sweden. The hexa-diagrams for the fresh and saline water are given in Fig. 2.1. The pH value of each classified groundwater varies from neutrality to alkalinity, and the Eh value indicates reducing environment. The concentrations of the dissolved elements for the fresh water are much lower than those for the saline water.

Most of the reported chemical properties in Japan were measured in comparatively shallow sedimentary layer formed in Quaternary and Neogene period[13]-[20]. The data measured in the depth over 50m were intended for the investigation of natural groundwater in Japan. On account of few measurements on the redox-potential (Eh) in Japan, the data, which was judged from the quantity of dissolved O_2 and the ratio of Fe(II) / total Fe, were treated as the reducing groundwater in Japan. The total number of the chemical properties investigated in Japan amounts to 102. The range of the collected data is shown in Table 2.3. Fig. 2.2 shows the hexa-diagram obtained from the property survey in Japan. The average concentration of the dissolved elements in the fresh water in Japan is hardly different from that in Sweden. The characteristic of the hexa-diagrams for the fresh water in Japan is almost consistent with one in Sweden as shown in Fig.

Table 2.2 Average values and range of chemical compositions measured in granitic rock in Sweden[11][12]

Measured chemical compositions of natural groundwater in Sweden			
Type of water		Saline water	Fresh water
Depth	m	329 (89~860)	500 (71~860)
pH		8.0 (7.3~9.0)	7.7 (6.9~8.2)
Eh	mV	-251 (-350~50)	-259 (-350~40)
Na^+	mg/l	1341 (300~3902)	30.3 (9.5~65)
K^+	mg/l	8.1 (1.3-19)	1.8 (1-3.2)
Ca^{2+}	mg/l	1117 (40~4400)	27.4 (8.3~76)
Mg^{2+}	mg/l	62.6 (0.2~250)	3.2 (1~6.3)
HCO_3^- (total)	mg/l	107.7 (10.4~285)	129.6 (78~220)
Cl^-	mg/l	4058 (470~13000)	23.9 (1.5~61)
F^-	mg/l	0.8 (0.55~1.1)	2.32 (<2.32)
SO_4^{2-} (total)	mg/l	253 (0.14~720)	2.1 (0.05~8.3)
NO_3^- (total)	mg/l	0.043 (<0.2)	0.05 (<0.1)
PO_4^{3-} (total)	mg/l	0.034 (<0.14)	0.05 (<0.1)
SiO_2 (total)	mg/l	7.2 (3.1~11.8)	7.1 (6.2~8)
Fe (total)	mg/l	0.69 (0.005~5.3)	1.16 (0.013~9)
Fe^{2+}	mg/l	0.68 (0.004~5.3)	1.14 (0.012~8.9)
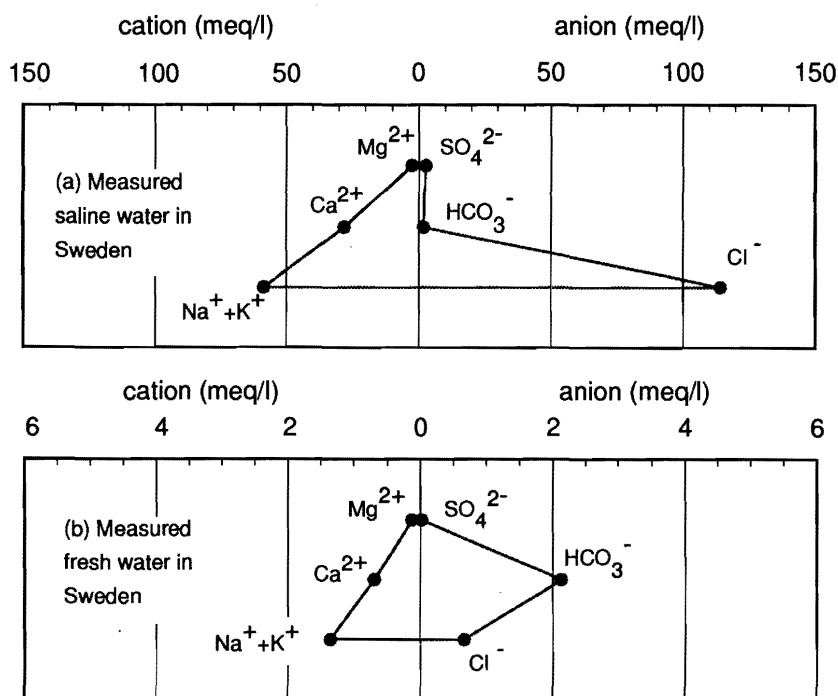
Fig. 2.1 Hexa-diagram for saline and fresh water in Sweden

2.2. As compared between two hexa-diagrams of the saline water, however, the concentration of each ion in Japan is much lower than that in Sweden. The saline groundwater in Sweden, which are isolated in granitic rock for long-term periods, contains a large quantity of NaCl at high pH, while the quantity of NaCl including in the saline water of neutral pH in Japan is not so high. Therefore, it is inferred that the saline water in Sweden belongs to the type of Na・Ca-Cl (Type C) and one in Japan is close to the type of Na・Ca-Cl・SO_4 (Type D) as shown in Table 2.1. The saline water in Japan is also characterized by the high concentration of SiO_2 because the main geological features corresponds to igneous rock and Tertiary rock.

Table 2.3   Average values and range of chemical compositions estimated from the measured groundwater in Japan[13]-[20]

Measured chemical compositions of natural groundwater in Japan			
Type of water		Saline water	Fresh water
Depth	m	110 (54~171)	119 (50~397)
pH		6.9 (6~7.5)	7.4 (6~9.1)
Na^+	mg/l	118 (18.2~734)	25.7 (3.7~107)
K^+	mg/l	6.6 (2.1~21.2)	2.4 (0.17~12.4)
Ca^{2+}	mg/l	41.0 (20~78)	15.7 (0.7~47.7)
Mg^{2+}	mg/l	25.6 (4.5~135)	4.4 (<17.4)
HCO_3^- (total)	mg/l	152 (43~394)	110 (16.5~308)
Cl^-	mg/l	248 (19~1742)	14 (0.9~85)
F^-	mg/l	0.7 (−)	3.9 (−)
SO_4^{2-} (total)	mg/l	45 (0.5~365)	6.6 (<34)
NO_3^- (total)	mg/l	1.7 (<6.9)	1.2 (<16)
PO_4^{3-} (total)	mg/l	0.15 (<0.58)	0.3 (<1.5)
SiO_2 (total)	mg/l	40.8 (27~53)	43 (11.3~81)
Fe (total)	mg/l	3.6 (0.05~7.3)	1.3 (0.02~6.1)
Fe^{2+}	mg/l	3.5 (0.04~7.3)	1.1 (0.01~6)
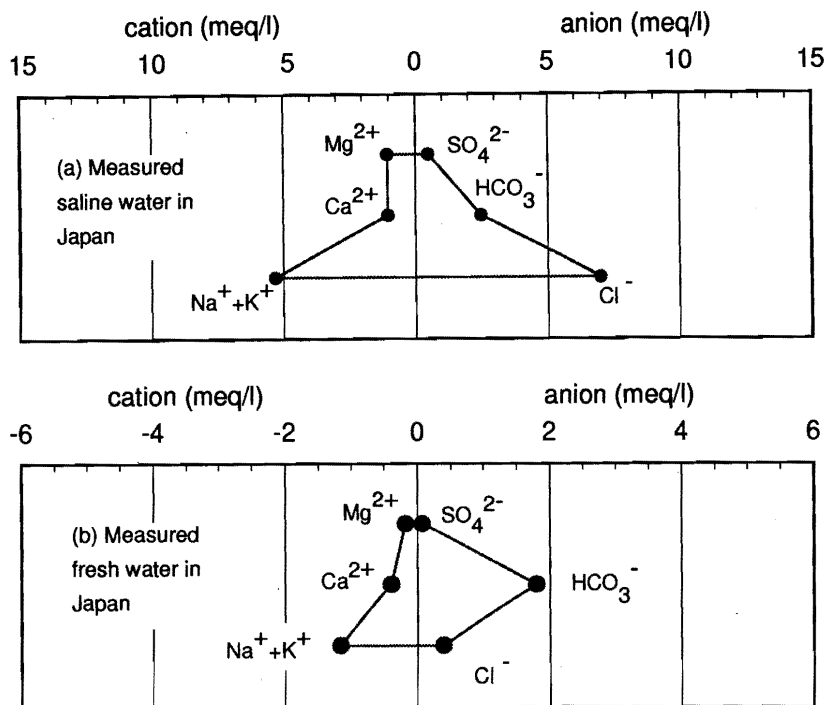
Fig. 2.2   Hexa-diagrams for saline and fresh water in Japan

2. 1. 2   Chemical property in buffer materials

The chemical characteristic of water in an engineered barrier is expected to be different from that of natural groundwater in geosphere because groundwater chemistry in an engineered barrier is controlled by the chemical interaction between natural water and buffer materials over long time periods. In order to understand the characteristic of the interstitial water in bentonite, experimental and modelling studies have been performed. Snellman, M.(1987)[21] examined the change of the synthetic groundwater in contact with sodium bentonite under the reducing condition. This result after 540 days is shown in Table 2.4. They reported that pH value shifted to alkalinity and Eh value dropped as the experimental time passed. They suggested that the concentrations of Na^+ and HCO_3^- increase according to the equilibrium with sodium bentonite. Table 2.4 also shows chemical property of bentonite interstitial water modeled by Curti, E. (1993)[7]. The property of bentonite interstitial water was calculated using alternatively two redox-controlling assemblages, based on two measured properties. One redox-potential was controlled by the ternary equilibrium of pyrite-magnetite-hematite, and the other Eh value was calculated by assuming the equilibrium of magnetite-goethite. The chemical properties in bentonite interstitial water were stimated from cation exchange model between solution and clay minerals. The chemical composition of the bentonite water in equilibrium with pyrite-magnetite-hematite is given in Table 2.4. The range of the property shown in Table 2.4 is based on four results calculated by Curti, E.. The estimated pH value is alkaline and the Eh value is

Table 2.4   Chemical compositions of bentonite water, measured by Snellman, M.(1987)[21] and simulated by Curti, E.(1993)[7].

reference		Chemical composition of bentonite water measured by Snellman,M.1987.	Modelled composition of bentonite pore water according to Curti, E. 1993.
pH		9.2	9.0 (8.5~9.0)
Eh	mV	-300	-397 (-397~105)
Na^+	mg/l	251	1803 (1785~5520)
K^+	mg/l	2.7	6.5 (6.4~22)
Ca^{2+}	mg/l	11.3	0.43 (0.43~2.2)
Mg^{2+}	mg/l	3.7	1.6 (1.6~1.7)
HCO_3^- (total)	mg/l	400	3096 (1104~3096)
Cl^-	mg/l	66	107 (107~6639)
F^-	mg/l	0.5	13.3 (3.6~13.3)
SO_4^{2-} (total)	mg/l	6	432 (432~1555)
PO_4^{3-} (total)	mg/l	0.8	0.15 (0.15~0.18)
SiO_2 (total)	mg/l	15	24.6 (17.7~24.6)
Fe (total)	mg/l	0.08	0.00002 (<0.00002)

calculated to be about -400mV. High Eh value of +105mV was obtained from the equilibrium modelling of magnetite-goethite. The tendency that the concentrations of Na^+ and HCO_3^- is comparatively high is qualitatively consistent with that in measurements by Snellman, M..

With respect to experimental and modelling studies on interaction between water and cement materials, the remarkable chemical properties in water-cement system are high pH and high Ca concentration [Atkinson, A. et al. (1985)[22] and Berner, U. (1990)[23]]. Atkinson, A. et al. (1985)[22] has estimated the time dependance of pH within the repository using their simple mass transfer model and equilibrium data in $CaO-SiO_2-H_2O$ (C-S-H) i.e., calcium-silicate-hydrates system. Their modelling of leaching behavior for cement materials depends on a Ca/Si molar ratio. The decreasing pH value with time was evaluated from the dissolution controlled by solid phase of $Ca(OH)_2(s)$ and $CaO-SiO_2-H_2O$ as a function of Ca/Si ratio. In their prediction, the evaluated pH would be maintained above 10.5 for about 4×10^6 years, and the maximum pH value was calculated to be about 13. Berner, U. (1990)[23] also has indicated the thermodynamic modelling of the cement property. The incongruent solubility behavior of C-S-H was described using the simplified equilibrium model. In his model, the leaching property of cement was controlled by the dissolution of three solid phases on hydrated calcium silicates. Apparent solubility products for these solid phases were given as a function of Ca/Si ratio. He also predicted the high pH level up to 13 in interstitial water. With respect to the experimental studies for

leaching behavior of cement paste, Anderson, K. et al. (1984)[25] measured the chemical property in interstitial water squeezed from ordinary portland cement (OPC) paste with water/cement ratio of 0.4. Mihara, M. et al. (1997)[26] also carried out the leaching experiments of cement paste to investigate effects of including the silica into cement and measured the chemical property. However, no Eh data in C-S-H system has been indicated by previous studies.

2. 2 Establishment of groundwater for analyses

As mentioned above, chemical property of groundwater in a disposal system is determined from several chemical reactions between natural groundwater and minerals, and has qualitative tendency on pH, Eh and concentration of dissolved ions. In order to estimate the effects of the chemical properties in groundwater on solubility and dominant aqueous species for radioactive elements, 10 kinds of the reducing groundwater as follows are assumed with the basis of the groundwater survey.

● case A : Saline water in Japan (indicated in Table 2.3).
● case B : Fresh water in Japan (indicated in Table 2.3).
● case C : Interstitial water in bentonite (according to Curti, E.(1993) in Table 2.4).
● case D : Groundwater in pH range of 6.0 to 13.0 at constant Eh-200mV.
● case E : Groundwater in Eh range of -200 to +200mV at constant pH6.0.
            : Interstitial water in bentonite in Eh range of -400 to +100mV at constant pH9.0.
● case F : Groundwater assuming various concentration of CO_3^{2-} ligand.
● case G : Groundwater assuming various concentration of PO_4^{3-} ligand.
● case H : Groundwater assuming various concentration of F^- ligand.
● case I : Groundwater assuming various concentration of SO_4^{2-} ligand.
●case J : Interstitial water in cement assuming various concentration of NO_3^- or NH_4^+ ligand.

The chemical properties of the groundwater in case A to case J are listed in Table 2.5. The values of chemical properties of groundwater for cases A and B is are the average values for saline and fresh water in Japan, respectively. Few Eh measured for Japanese groundwater is available, so the value is -200mV based on the Eh measurements in Sweden. The bentonite interstitial water of case C in an engineered barrier is established from the simulated property according to Curti, E.(1993)[7]. This bentonite water indicates the tendency that the concentrations of Na^+ and HCO_3^- are comparatively high. The chemical property is qualitatively consistent with that in measurements by Snellman, M. as discussed in Section 2.1.2. Seven kinds of the groundwater of case D to case J are used in order to estimate the effect of pH, Eh and the concentrations of the dissolved ions. The chemical properties in case D to case J are not independently determined from change of noticed chemical condition, but from equilibrium

Table 2.5 Chemical compositions of the groundwater of case A to case J used in analyses

case		case A	case B	case C	case D	case E		case F	case G	case H	case I	case J
pH		6.9	7.4	9.0	6.0 ~13.0	6.0	9.0	8.0 ~13.0	6.0 ~8.0	6.0 ~8.0	6.0 ~8.0	8.0 ~13.0
Eh	mV	-200	-200	-397	-200	-200 ~+200	-400 ~+100	-100 ~ -400	-200 ~ -50	-200 ~ -50	-200 ~ -50	-400 ~ -100
Na^+ (total)	mg/l	118	25.7	1803	25.7	25.7	1803	33.7	18.1	18.1	118	23
K^+ (total)	mg/l	6.6	2.4	6.5	2.4	2.4	6.5	1.6	2.1	2.1	6.6	39
Ca^{2+} (total)	mg/l	41.0	15.7	0.43	15.7	15.7	0.43	1.8	18	18	41.0	800
Mg^{2+} (total)	mg/l	25.6	4.4	1.6	4.4	4.4	1.6	0.6	3.7	3.7	25.6	2.0
HCO_3^- (total)	mg/l	152	110	3096	110	110	3096	6.1 ~3100	62.2	62.2	152	6.1 ~3100
Cl^- (total)	mg/l	248	14	107	14	14	107	5.1	17.5	17.5	248	20
F^- (total)	mg/l	0.7	3.9	13.3	3.9	3.9	13.3	0.7	0.1	0.019 ~190	0.7	-
SO_4^{2-} (total)	mg/l	45	6.6	432	6.6	6.6	432	10.4	24.3	24.3	0.96 ~2880	200
NO_3^- (total)	mg/l	1.7	1.2	—	1.2	1.2	—	—	—	—	1.7	0.05 ~3100
PO_4^{3-} (total)	mg/l	0.15	0.3	0.15	0.3	0.3	0.15	0.3	0.095 ~950	0.1	0.15	-
SiO_2 (total)	mg/l	40.8	43	24.6	43	43	24.6	62	42	42	40.8	30
Fe (total)	mg/l	3.6	1.3	0.00002	1.3	1.3	0.00002	0.1	5.4	5.4	3.6	-

witth the other chemical conditions. In case D, the range of pH change used in this analysis is assumed to vary from 6.0 to 13.0 at constant Eh-200mV. This pH range is determined from the result of groundwater survey. The chemical property besides pH value in case D is cited from one of the data for fresh water in Japan. The influence of redox-potential on solubility and speciation was estimated from the analyses in case E. The calculation for the Eh change is carried out under two pH conditions, pH6.0 and 9.0. The redox-potential in bentonite interstitial water, according to Curti, E. in Table 2.4, has been predicted to increase up to about +100mV. Based on his modelling results, the Eh range of the bentonite water used here is assumed to be from -400 to +100mV at pH9.0. The Eh measurements in Sweden as shown in Table 2.2 indicates the upper limit of Eh+50mV. The Eh range at pH6.0 was established to be from -200 to +200mV, taking account of a slightly higher Eh value than +50mV.

The concentrations of ligands with complexation may also have an effect on solubility and speciation of radioactive elements. The main aqueous species in a solution are considered to be hydroxide, carbonate, phosphorus, sulphur, fluoride, chlorine, nitrate complexes and so on. The ligands needed for the formation of these aqueous species are OH^-, CO_3^{2-}, F^-, PO_4^{3-}, SO_4^{2-}, Cl^-, NO_3^-, and so on. The trend in strengths of the complexation of these ligands may slightly vary with radionuclides, and the general trend has been indicated by Silva, R. J. and Nitsche, H. (1995)[27] as follows.

$$OH^-, CO_3^{2-} > F^-, PO_4^{3-}, SO_4^{2-} > Cl^-, NO_3^-$$
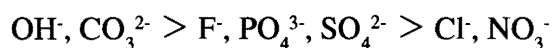
The ligands with respect to the dominant complexation are especially supposed to be CO_3^{2-}, F^-, PO_4^{3-} and SO_4^{2-}, from this trend in strengths of the complexation. The relation between the concentration of these ligands and solubilities for radioactive elements is examined from the calculations in case F to case I, assuming various concentration of each ligand. The groundwater of case F was cited from one property belonging to the $Na-HCO_3$ type measured at high pH in Japan because the influence of CO_3^{2-} may appear to be more remarkable at alkaline pH. The carbonate concentration used in analysis ranges from 6.1 to 3100mg/l (1×10^{-4} to 5×10^{-2}mol/l) as shown in Table 2.5. Two kinds of the groundwater, case G and case H, assuming various concentrations of PO_4^{3-} and F^- were based on a chemical property measured at weak acid pH in Japan. The concentrations of PO_4^{3-} and F^- vary from 0.095 to 950mg/l (1×10^{-6} to 1×10^{-2}mol/l) and from 0.019 to 190mg/l (1×10^{-6} to 1×10^{-2}mol/l), respectively. The concentration of SO_4^{2-} is considered to be high in saline water, so that the groundwater of case I based on the assumption of various concentration of SO_4^{2-} is established from the property of the saline water shown in Table 2.3. The sulphur concentration used in calculation is assumed to be in the range of 0.96 to 2880mg/l (1×10^{-5} to 3×10^{-2}mol/l). It is considered that the effect of OH^- and CO_3^{2-} on strong complexation gradually tends to grow down with decreasing pH. Therefore, the calculations for various concentrations of PO_4^{3-}, F^- and SO_4^{2-} are particularly performed under acid or neutral pH

condition.

In the case of waste dispersal from reprocessing cycle, it is considered that the chemical property in a buffer material may be effected by the dissolution of NO_3^- owing to leaching from waste matrix, bituminized radioactive waste, including a large quantity of $NaNO_3(s)$. The calculation for case J examined the influence of nitrogen concentration from bituminized waste in cement buffer materials. Akimoto, T., Nakayama, S. et al. (1999)[28] made a literature survey on leachability of bituminized radioactive waste. In their report, the leachability of bituminized waste especially depends on a type and quantity of salts including in bituminized waste. High salt concentration causes the deterioration of bituminized matrix, so that it enhances the leach rate. From comparison of leach tests for bitumen and cement, the leach rates of Na and ^{137}Cs in bitumen is about 2 order of magnitude lower than those in cement [IAEA (1970)][29]. From the lower leach rate of bitiumen, it is assumed that the chemical property used in case J was basically controlled by cement buffer materials. The chemical properties without nitrogen concentration were determined from the experimental and modelling data for cement materials[23]-[26]. Nitrogen concentration enhanced by the dissolution of $NaNO_3(s)$ was treated as the possible range in case J. There is no previous study on the dissolution of NO_3^- from bituminized waste matrix in reducing environment[28]. Taking account of the lower leach rate of Na in bitumen than in cement, the possible upper limit of nitrogen concentration was conservatively assumed to be 2×10^{-2} mol/l based on the solubility of $Ca(OH)_2(s)$ which indicates the highest solubility in

Table 2.6　Possible range of pH, Eh and ligand concentrations determined from investigation on natural groundwater and interstitial water in buffer materials (bentonite and cement)

parameters	Possible Ranges
pH	$6.0 \sim 13.0$
Eh	$-200 \sim +200$mV (pH6.0) $-400 \sim +100$mV (pH9.0)
HCO_3^-(total)	$10\sim3100$mg/l $(1.6\times10^{-4}\sim5.0\times10^{-2}$mol/l)
PO_4^{3-}(total)	$0.0001\sim1.5$mg/l $(1.0\times10^{-10}\sim1.6\times10^{-5}$mol/l)
F^-	$0.5\sim13.3$mg/l $(2.6\times10^{-5}\sim7.0\times10^{-4}$mol/l)
SO_4^{2-}(total)	$0.05\sim1550$mg/l $(5.2\times10^{-7}\sim1.6\times10^{-2}$mol/l)
NO_3^-(total)	$0.05\sim1240$mg/l $(8.1\times10^{-7}\sim2.0\times10^{-2}$mol/l)

calcium-silicate-hydrates system as mentioned in section 2.1.2. The lower limit was determined from the groundwater survey. The analyses for nitrogen concentration in case J were carried out under various conditions of Eh-pH and carbon concentration.

It was assumed that the divergence of charge balance on calculations from case A to case J is revised by Na^+ or Cl^-. The influence of the ligand concentrations on solubility and speciation for radioactive elements should be estimated within possible range of their concentrations. Therefore, the possible range of each ligand was decided from the investigation of chemical property. Table 2.6 shows the possible range of pH, Eh and the concentration of each ligand determined from investigation on groundwater and interstitial water in buffer materials. As mentioned above, the possible range of nitrogen concentration is assumed to be restricted by the solubility of $Ca(OH)_2(s)$. The sensitivity of solubility and speciation to various chemical property is estimated under this possible condition of Eh, pH and ligand concentration.

3. Thermodynamic Data

Thermodynamic data has been provided in the data base by Yamaguchi, T. and Takeda, S (1998)[9]. This data base is used in this solubility and speciation analysis. The summary of selected thermodynamic data for americium, plutonium and technetium are indicated in the following section.

3.1 Americium thermodynamic data

Americium has oxidation states ranging from III to VI. The Nuclear Energy Agency (NEA) indicated the reliable thermodynamic data of americium from the review of the published data[28]. The americium thermodynamic data from III to VI are mostly cited from the NEA data base. The NEA has established only the thermodynamic data for the chemical species having certain experimental evidence that can prove their existence. According to the concentration level for ligand complexation, it is supposed that there are several species of which the formation can not be ignored for chemical property in disposal site. Therefore, taking account of the latest thermodynamic data and the effect of ligand concentration discussed in section 2, the data of americium(III) hydroxy-carbonate, nitrate, ammoniate and sulphate complexes have been added in JAERI-data base[9]. The americium thermodynamic data used here are listed in Table A1 of appendix.

Several experimental studies have concluded that the experimental results in carbonate media can be interpreted with the assumption that only americium(III) carbonate complexes and hydrolysis products are formed. Based on this conclusion, the equilibrium constants of americium (III) hydroxide-carbonate complexes i.e., $AmOHCO_3(aq)$, $Am(OH)_2CO_3^-$ and $AmOH(CO_3)_2^{2-}$, are not presented in the NEA review[30]. The NEA also indicates that further experimental work
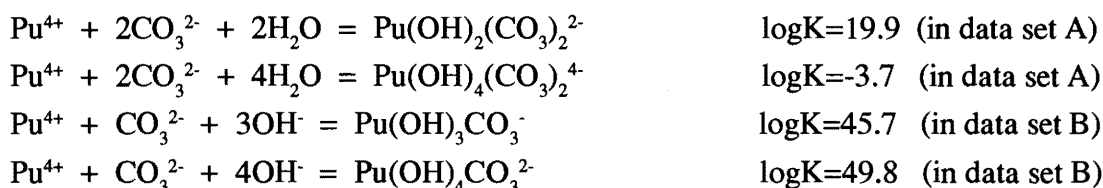
is needed to confirm or deny the existence of these species in aqueous solutions. In the review of Yamaguchi, T. and Nakayama, S. (1996)[31], however, some experimental data reported previously can be more rationally reinterpreted assuming the existence of hydroxide-carbonate complexes, so that the formation of americium(III) hydroxide-carbonate complexes is supported. The stability constants of americium(III) hydroxide-carbonate complexes, $AmOHCO_3(aq)$, $Am(OH)_2CO_3^-$ and $AmOH(CO_3)_2^{2-}$, according to Yamaguchi, T. and Nakayama, S. (1996) are established in this data base.

With respect to $Am(NO_3)_n^{3-n}$ (n=1 to 6), only the data of $AmNO_3^{2+}$ has been accepted in NEA review owing to the agreement with some reviewed experimental data. The formation of $Am(NO_3)_n^{3-n}$ (n=2, 3) was also pointed out by only the experimental study performed by Lahr, H. (1970)[30]. The NEA rejected the equilibrium constants of $Am(NO_3)_n^{3-n}$ (n=2, 3) obtained at high concentration of HNO_3 solution because of the problem on accurate extrapolation to zero ionic strength. Brown, P. L. and Wanner, H.(1987)[33] predicted the data of $Am(NO_3)_n^{3-n}$ (n=1 to 6) using the unified theory of metal ion complex formation constants. Taking account of the effect of nitrate ion leaching from waste matrix, the existence of $Am(NO_3)_n^{3-n}$ (n=2 to 6) is also assumed in this data base, according to Brown, P. L. and Wanner, H.(1987). The NEA review selected no data of americium ammoniate complexes, $Am(NH_3)_n^{3+}$ (n=1 to 6), and sulphate complexes, $Am(SO_4)_n^{3-2n}$ (n=3 to 5). Judging from importance on the formation of these complexes as well as nitrate complexes, the data obtained from Brown, P. L. and Wanner, H.(1987) are considered in this data base.

3. 2 Plutonium thermodynamic data

Plutonium thermodynamic data in the oxidation state of III to VI have been indicated in many reports, such as Nitsche, H. (1991)[34], Puigdomenech, I. (1991)[35], Robert, J. and Lemire, R. J. (1989)[36], IAEA (1992)[37]. Based on these previous data base, Yamaguchi, T. and Takeda, S (1999)[9] decided temporary thermodynamic data of plutonium. Table A2 of the Appendix shows the selected data and their references. This data base considers the data of both plutonium (IV) carbonate and hydroxide-carbonate complexes. The experimental studies with respect to plutonium(IV) carbonate or hydroxide-carbonate complexes have been reported by Kim, J. I. (1983)[38], Lierse, C. and Kim, J. I.(1986)[39], Yamaguchi, T.(1994)[40] and Nitsche, H.(1996)[41]. Several authors have indicated that plutonium(IV) hydroxide-carbonate complexes are more dominant than carbonate complexes. Tait, C. D. et al. (1995)[42] pointed out the possibility of the existence of hydroxide-carbonate complexes from the results measured using photoacoustic absorption spectroscopy (PAS). However, their experiments were insufficient for the identification of hydroxide-carbonate complexes. The existence of hydroxide-carbonate complexes has been reported by Yamaguchi, T. et al. (1994)[40] and Eriksen,T. E. (1993)[43], but the estimated hydroxide-carbonate complexes are different among these two. Two kinds of data

set on plutonium(IV) hydroxide-carbonate complexes are assumed in the calculation owing to the uncertainty of the formation of plutonium(IV) hydroxide-carbonate complexes. The following equilibrium constants of $Pu(OH)_n(CO_3)_2^{n-}$ (n=2,4) obtained from Yamaguchi, T. et al. (1994) and $Pu(OH)_nCO_3^{2-n}$ (n=3,4) from Eriksen,T. E. (1993), is considered in data set A and data set B, respectively.

$$Pu^{4+} + 2CO_3^{2-} + 2H_2O = Pu(OH)_2(CO_3)_2^{2-} \qquad logK=19.9 \text{ (in data set A)}$$
$$Pu^{4+} + 2CO_3^{2-} + 4H_2O = Pu(OH)_4(CO_3)_2^{4-} \qquad logK=-3.7 \text{ (in data set A)}$$
$$Pu^{4+} + CO_3^{2-} + 3OH^- = Pu(OH)_3CO_3^- \qquad logK=45.7 \text{ (in data set B)}$$
$$Pu^{4+} + CO_3^{2-} + 4OH^- = Pu(OH)_4CO_3^{2-} \qquad logK=49.8 \text{ (in data set B)}$$

In order to estimate the reliable data on plutonium(IV) hydroxide-carbonate complexes, the solubility calculations using two data sets are compared with plutonium solubility measurements. The thermodynamic data of sulphate, nitrate and ammoniate complexes with plutonium(III) to (VI), which can not be taken from experiments, are based on the predicted data by Brown, P. L. and Wanner, H.(1987)[33].

3. 3 Technetium thermodynamic data

Rard, J. A. (1983)[44] estimated technetium thermodynamic data from experimental papers. The data base are referred by Isherwood, D.(1985)[45] and Robert, J. and Lemire, R. J.(1989)[36]. The latest thermodynamic data base has been indicated by Puigdomenech, I. (1995)[46]. The data base of Puigdomenech, I. (1995) is basically cited from the data of Rard, J. A. (1983). However, Lemire, R. J. and Jobe, D. J. (1996)[47] pointed out some arithmetic errors in the estimation of TcO_4^- thermodynamic data given by Rard, J. A. (1983). Yamaguchi, T. and Takeda, S (1999)[9] have recalculated thermodynamic data which should be revised account of the change of TcO_4^- thermodynamic data. The thermodynamic data selected in the data base of Yamaguchi, T. and Takeda, S (1999) is listed in Table A3 of appendix. This data base includes the thermodynamic data of technetium(IV) sulphate, nitrate and ammoniate complexes, predicted using the unified theory of metal ion complex formation constants by Brown, P. L. and Wanner, H.(1987)[33].

4. Americium Results

4. 1 Saline water (case A), fresh water (case B) and simulated bentonite water (case C)

First of all, the solid phase limiting americium solubility is examined through the solubility and speciation analysis for three kinds of the typical groundwater, saline water (case A), fresh water (case B) and simulated bentonite water (case C). The stable solid phases are considered to be $Am(OH)_3(c)$, $Am_2(CO_3)_3(c)$ and $AmOHCO_3(c)$. Table 4.1 shows the americium solubility and speciation for each solid phase in case A, case B and case C. The solubility of $AmOHCO_3$ (c) tends to be the lowest in all the solid phases. The stabilities of these americium solid phases depend on carbonate concentration in groundwater. The range of log Pco_2, in which each solid phase is stable, is calculated from each equilibrium constant as shown in Table 4.2. The logarithm of CO_2 partial pressure in each typical groundwater is also shown in Table 4.3. All the values of CO_2 partial pressure calculated in the groundwater of case A to case C lie within the Pco_2 range of $AmOHCO_3(c)$. It is considered that high solubilities of both $Am(OH)_3(c)$ and $Am_2(CO_3)_3(c)$ are impractical and the realistic solubility of americium is controlled by $AmOHCO_3(c)$ in each typical groundwater. The maximum solubility of $AmOHCO_3(c)$ amounts to 8.6×10^{-7} mol/l for the saline water (case A). The dominant aqueous species of americium were estimated to be

Table 4.1 Americium solubilities and speciation for saline water (caseA), fresh water (case B) and simulated bentonite water (case C)

Type of water	pH Eh (mV)	solubility (mol/l)			speciation (%)	
		$Am(OH)_3(c)$	$Am_2(CO_3)_3(c)$	$AmOHCO_3(c)$		
Saline water (case A)	6.9 -200	2.0×10^{-4}	3.0×10^{-6}	8.6×10^{-7}	$AmCO_3^+$ $AmOH^{2+}$ Am^{3+} $AmSO_4^+$ $AmOHCO_3$ $Am(CO_3)_2^-$ $Am(OH)_2^+$	70.0 14.1 5.4 4.7 2.9 1.1 1.0
Fresh water (case B)	7.4 -200	2.0×10^{-5}	1.6×10^{-6}	2.7×10^{-7}	$AmCO_3^+$ $AmOH^{2+}$ $AmOHCO_3$ $Am(CO_3)_2^-$ $Am(OH)_2^+$ Am^{3+}	69.3 12.1 9.5 3.3 3.0 1.2
Simulated bentonite water (case C)	8.9 -397	6.3×10^{-6}	7.5×10^{-6}	5.0×10^{-7}	$AmOH(CO_3)_2^{2-}$ $Am(OH)_2CO_3^-$ $Am(CO_3)_3^{3-}$ $Am(CO_3)_2^-$ $AmOHCO_3$ $AmCO_3^+$	43.3 19.2 17.2 14.0 5.1 0.9

Table 4.2 Range of log Pco$_2$ for Am solid phases calculated from equilibrium constants

Solid phase	log PCO2
Am(OH)3(c)	< -4.2
AmOHCO3(c)	-4.2 to -0.8
Am2(CO3)3(c)	> -0.8

Table 4.3 Calculated log Pco$_2$ in each typical groundwater

Type of water	Saline water (case A)	Fresh water (case B)	Simulated bentonite water (case C)
calculated log Pco2	-1.9	-2.4	-3.2

americium(III) carbonate complex in case A and case B. The formation ratio of AmCO$_3^+$ accounts for about 70% of americium aqueous species and the ratio of AmOH^{2+} exists over 10%. In alkaline groundwater (case C), all the dominant species are composed of americium(III) hydroxide-carbonate and carbonate complexes.

4. 2 Effect of pH and Eh conditions (case D and case E)

The effect of pH condition on americium solubility and speciation is evaluated from the calculation for the groundwater of case D. The variable pH value of 6.0 to 13.0 was assumed in the groundwater of case D under constant Eh condition of -200mV. Fig. 4.1 shows americium solubility and speciation as a function of pH in case D. Americium solubility is high at low pH condition and decreases with changing up to about pH8.0. The solubility profile goes up in the pH range of 8.0 to 9.0 and again goes down over 9.0. The solubility decreases to about 2x10^{-10} mol/l at pH13 owing to the americium solid phase changing from AmOHCO$_3$(c) to Am(OH)$_3$(c) with increasing pH. The solubility over pH8.0 depends on the concentration of Am(OH)$_2$CO$_3^-$. Cationic forms such as Am^{3+}, AmOH^{2+}, AmF^{2+} and AmCO$_3^+$ are dominant in low pH range. Americium aqueous phase consists of many chemical forms under acid and neutral pH condition. The dominant species change to Am(OH)$_2$CO$_3^-$ with increasing pH.

The groundwater of case E, assuming the constant pH and variable Eh, is used to estimate the effect of Eh condition at weak acid and alkaline pH. The Eh value is allowed to change from -200 to +200 mV at pH6.0. The Eh range at pH9.0 is assumed to be from -420 to +100 mV. The result of americium solubility at pH6.0 is shown in Fig. 4.2. The solubility of AmOHCO$_3$(c) is
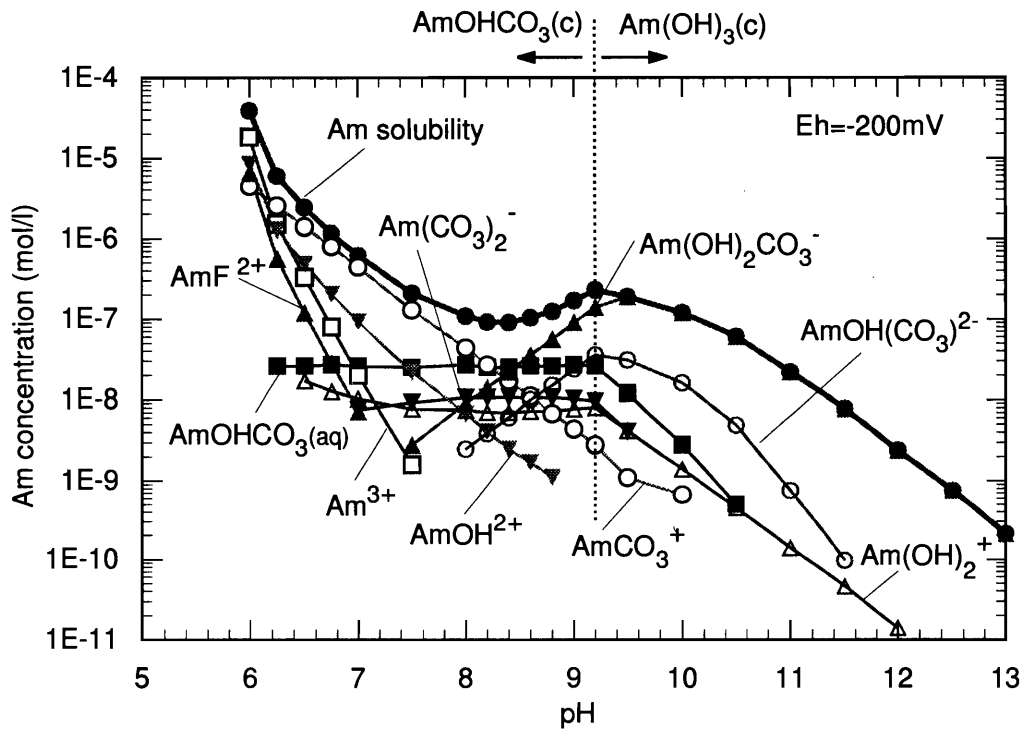
Fig. 4.1 Americium solubility and speciation for the groundwater (case D) assuming the constant Eh (-200mV) and the pH range of 6.0 to 9.0
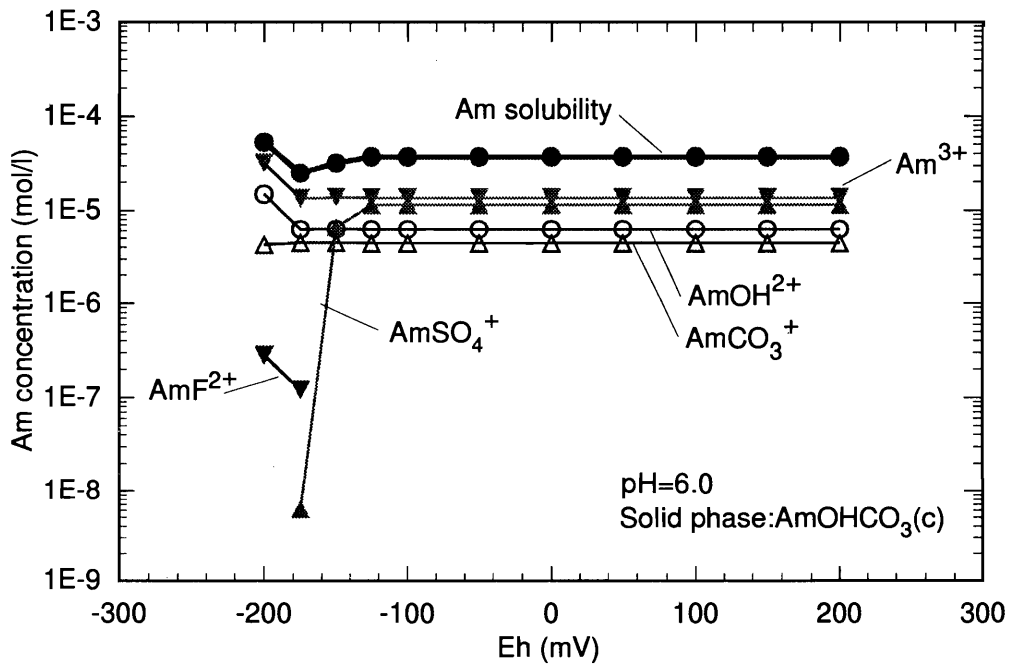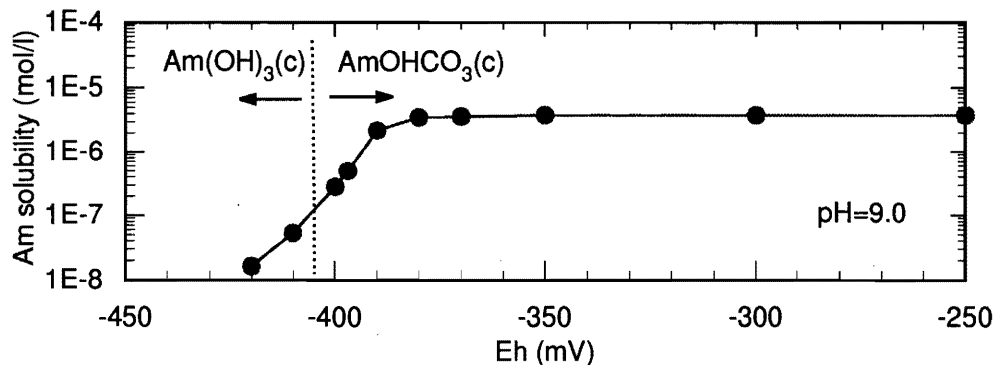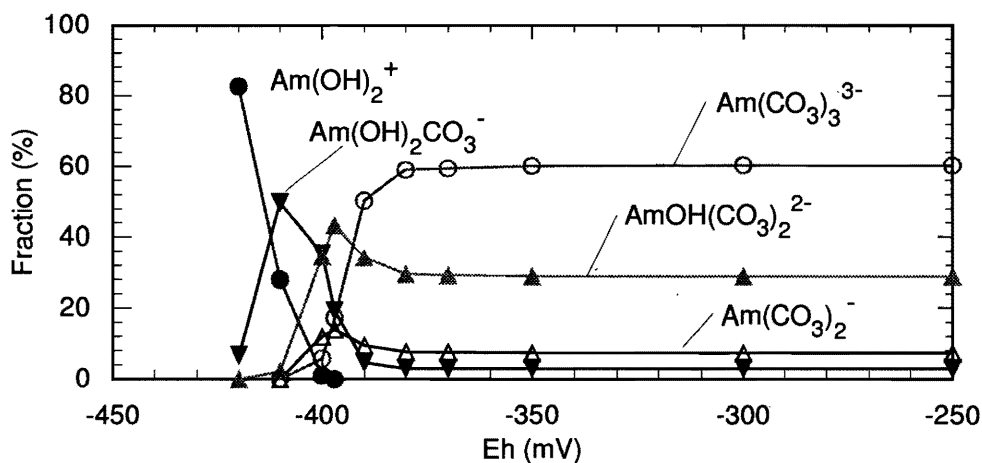

Fig. 4.2 Americium solubility and speciation for the groundwater (case E) assuming the constant pH6.0 and the Eh range of -200 to +200mV

estimated to be about 4×10^{-5} mol/l in the Eh range of -200 to +200mV. The dominant aqueous species are Am^{3+}, $AmSO_4^+$, $AmOH^{2+}$ and $AmCO_3^+$, but the concentration of $AmSO_4^+$ decreases under Eh-160mV. Because $H_2S(aq)$ or HS^- is more stable than SO_4^{2-} under Eh-160mV at pH6.0, americium(III) sulphur complex is hardly formed under this Eh condition. Fig. 4.3(a) shows the

(a) Am solubility

(b) Fraction of Am aqueous species
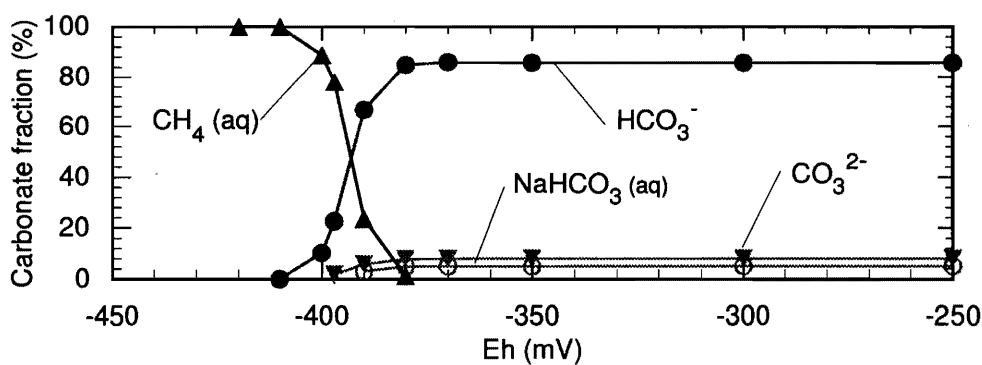
(c) Fraction of aqueous species for carbon

Fig. 4.3   Effect of the Eh condition on americium solubility and speciation at pH9.0

result of calculated solubility at pH9.0. The Eh change of -420 to -390 mV has an effect on the americium solubility. In respect of the solid phase limiting americium solubility, $Am(OH)_3(c)$ which is stable under the strong reducing condition of < -400mV changes into $AmOHCO_3(c)$ with increasing Eh. The solubility of $AmOHCO_3(c)$ is about two orders of magnitude higher than that of $Am(OH)_3(c)$. The change of americium aqueous species for Eh value is shown in Fig. 4.3(b). The predominant species of americium also vary at about -400mV. Americium(III) hydroxide complexes, $Am(OH)_2^+$, are transformed to americium(III) carbonate and hydroxide-carbonate complexes i.e., $Am(CO_3)_3^{3-}$ and $AmOH(CO_3)_2^{2-}$, with increasing Eh. As shown in Fig. 4.3(c), this transformation of americium dominant species depends on the change of carbon aqueous species. Under the low Eh condition of <-400mV, the formation of americium(III) carbonate complexes is not promoted because $CH_4(aq)$ is stable in this carbonate solution. The americium solubility increases on account of the formation of americium(III) carbonate and hydroxide-carbonate complexes. In the Eh range of -350 to +100mV, the solubility of $AmOHCO_3$ (c) is constant at 2.6×10^{-6} mol/l and not influenced by the redox-potential.

4. 3　Effect of various ligand concentration

4. 3. 1　Effect of CO_3^{2-} concentration (case F)

Several experimental studies have concluded that the experimental results in carbonate media can be interpreted with the assumption that only americium(III) carbonate complexes and hydrolysis products are formed. Based on this conclusion, the equilibrium constants of americium (III) hydroxide-carbonate complexes i.e., $AmOHCO_3(aq)$, $Am(OH)_2CO_3^-$ and $AmOH(CO_3)_2^{2-}$, were not established in the NEA (1995)[30] data base. The NEA (1995) also reported that further experimental work was needed to confirm or deny the existence of these species in aqueous solutions. In the review of Yamaguchi, T. and Nakayama, S. (1996)[31], however, experimental data could be more rationally reinterpreted assuming the existence of hydroxide-carbonate complexes, so that the formation of americium(III) hydroxide-carbonate complexes was supported. Based on their conclusion, the thermodynamic data base in this study takes account of the data of both americium carbonate and hydroxide-carbonate complexes.

The effect of carbonate concentration in a solution is analysed for case F for various carbonate concentrations of 1×10^{-4} to 5×10^{-2} mol/l. The Eh-pH dependance for the complexation of carbon is also investigated in this calculation. Figure 4.4 shows the pH dependance of the americium solubility at Eh-200mV and the total carbon concentration of 5×10^{-2} mol/l. This solubility result can be compared with that in case D as shown in Fig. 4.1. In alkaline pH region, the maximum solubility in case F is approximately two orders of magnitude higher than that in case D because of the higher carbon concentration (5×10^{-2} mol/l) in case F. The pH condition indicating the peak solubility in case F shifts to more alkaline (pH10). The Eh change from -400
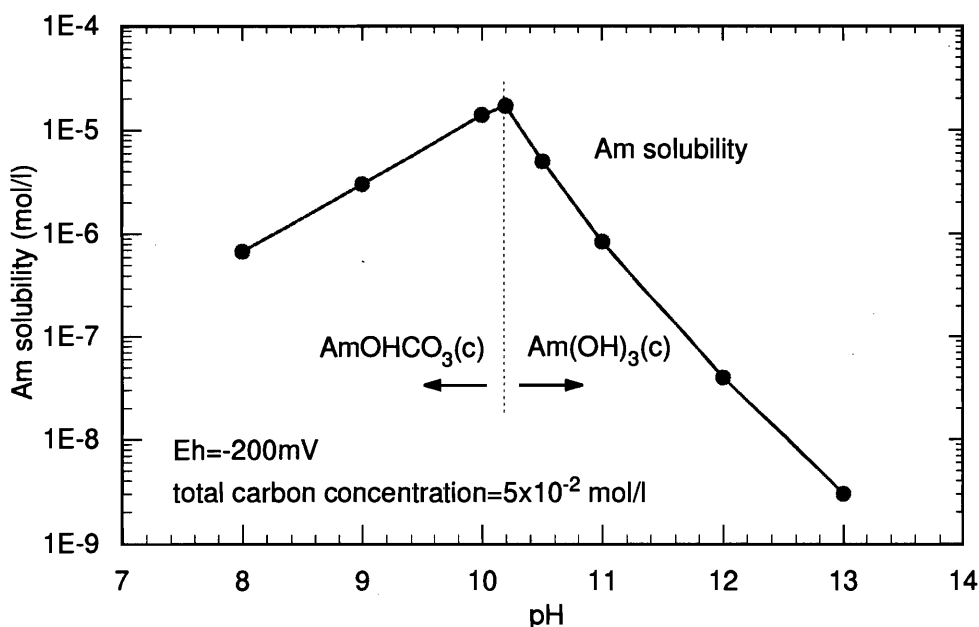
Fig. 4.4 pH dependance of the americium solubility at Eh-200mV and total carbon concentration of 5×10^{-2} mol/l

to -100mV has no effect on the solubility curve at the pH range of 8.0 to 13.0. In high pH condition controlled by the dissolution of cement materials, the solubility profile in the pH range of 10.0 to 13.0 indicates the change by about four orders of magnitude. This decrease in solubility is based on the change of solid phase from $AmOHCO_3(c)$ to $Am(OH)_3(c)$.

Figure 4.5 (a) and (b) show the americium solubility and speciation at pH9.0 and 10.0, respectively, as a function of the total carbon concentration. In accordance with increasing carbon concentration from 1×10^{-4} to 5×10^{-2} mol/l, the solubility at pH9.0 rises from 3.2×10^{-8} to 2.9×10^{-6} mol/l and at pH10.0 increases from 8.0×10^{-9} to 1.5×10^{-5} mol/l. It is suggested that americium solubility at alkaline pH is strongly dependent on pH value and carbon concentration in a solution. With respect to americium solid phase limiting solubility, $Am(OH)_3(c)$ changes into $AmOHCO_3(c)$ at pH9.0 at comparatively low carbon concentration of $> 7 \times 10^{-4}$ mol/l, but at pH10.0 at high carbon concentration of $> 2 \times 10^{-2}$ mol/l. In this range of carbon concentration, americium aqueous phase almost consists of carbonate and hydroxide-carbonate complexes at alkaline pH. In accordance with increasing carbon concentration, americium dominant species changes as follows, based on both the results at pH9.0 and 10.0.

$$Am(OH)_2CO_3^- \rightarrow AmOH(CO_3)_2^{2-} \rightarrow Am(CO_3)_3^{3-}$$

The maximum carbonate concentration estimated from the investigated chemical composition data amounts to 5×10^{-2} mol/l. If this carbonate concentration limit is allowed in chemical composition, americium solubility is suggested to increase up to about 1.5×10^{-5} mol/l with increasing carbon concentration. This maximum solubility effected by carbon concentration
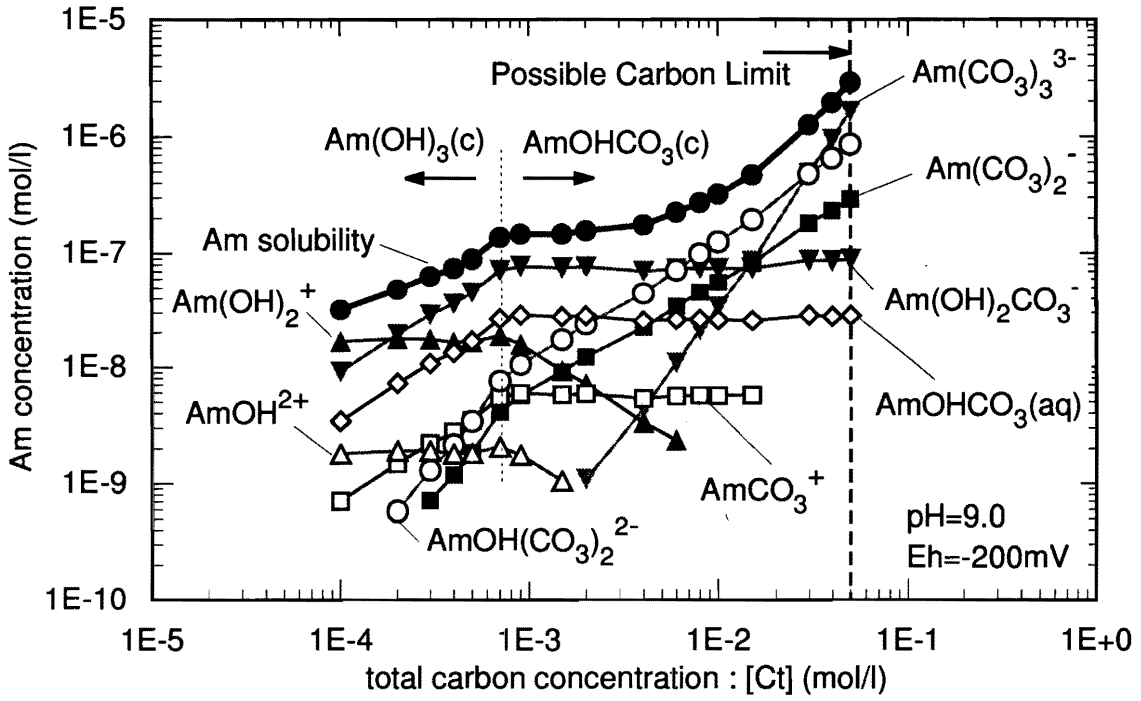
(a) pH9.0
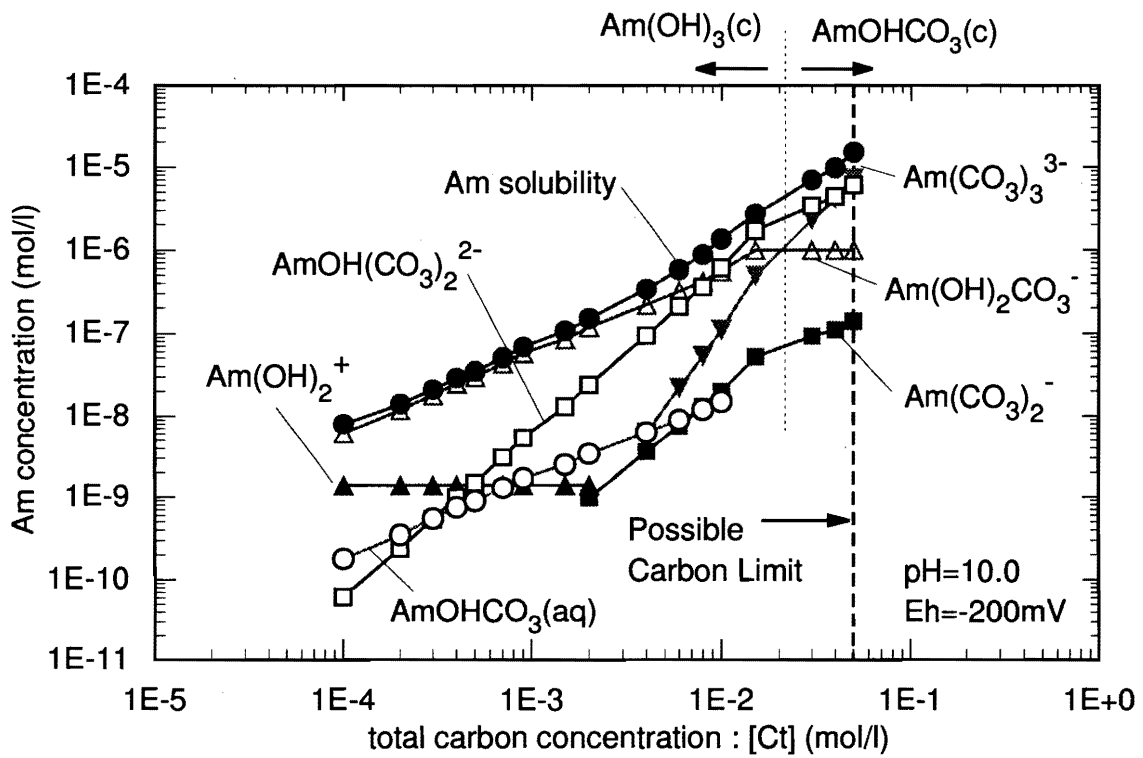
(b) pH10.0

Fig. 4.5   Effect of carbonate concentration on americium solubility and speciation.
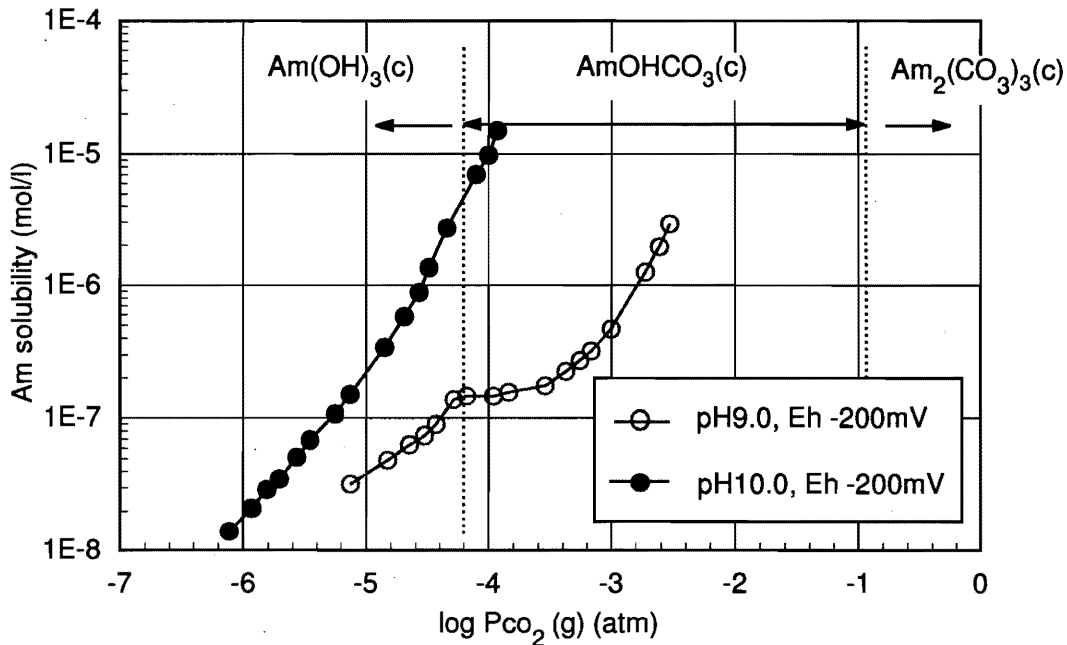
Fig. 4.6 Relation between the calculated CO_2 partial pressure and the solubilities at pH9.0 and 10.0

is analyzed at pH10 and carbon concentration of 5×10^{-2} mol/l. The relation between the calculated CO_2 partial pressure and the solubilities at pH9.0 and 10.0 is shown in Fig. 4.6. The logarithm of CO_2 partial pressure is estimated to be about -2.5 atm at pH9.0 and carbon concentration of 5×10^{-2} mol/l. If the stable solid phase at alkaline pH changes into $Am_2(CO_3)_3$ (c), carbon concentration in groundwater must be quite higher than the possible carbon concentration of 5×10^{-2} mol/l. It is considered that $Am(OH)_3(c)$ or $AmOHCO_3(c)$ is appropriate to the solid phase limiting americium solubility in the possible carbon concentration range.

4. 3. 2　Effect of PO_4^{3-} concentration (case G)

The thermodynamic data for $Am(H_2PO_4)_n^{3-n}$ (n=1, 2, 3) are considered in this data base. The Eh-pH dependence of the formation of $Am(H_2PO_4)_n^{3-n}$ (n=1, 2, 3) is examined under some Eh-pH conditions. The phosphorus concentration ranges from 1×10^{-6} to 1×10^{-2} mol/l. Figure 4.7 shows total fraction of americium(III) phosphorus complexes at pH6.2, 6.5 and 6.8. The formation of $Am(H_2PO_4)_n^{3-n}$(n=1, 2) is promoted with increasing phosphorus concentration at these Eh-pH conditions. The increase of the fraction is striking under the lower pH condition. The fraction drops under 10 % at the higher pH7.0. The formation of americium(III) phosphorus complexes dose not change in the Eh range of -200 to -50mV. Fig. 4.8 shows the americium speciation at pH6.2 and Eh-200 mV, indicating the most remarkable effect of phosphorus complexes. At the phosphorus concentration of $< 1 \times 10^{-3}$ mol/l, the solubility of $AmOHCO_3(c)$ is constant, and the dominant aqueous species is estimated to be Am^{3+} and $AmOH^{2+}$. However, if
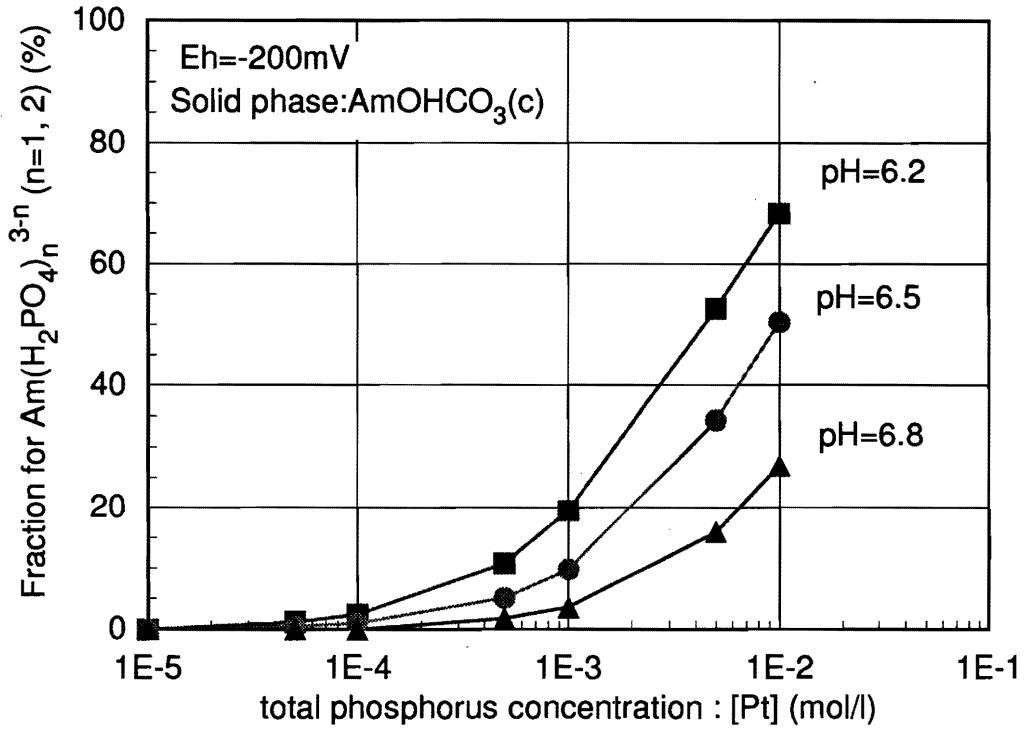
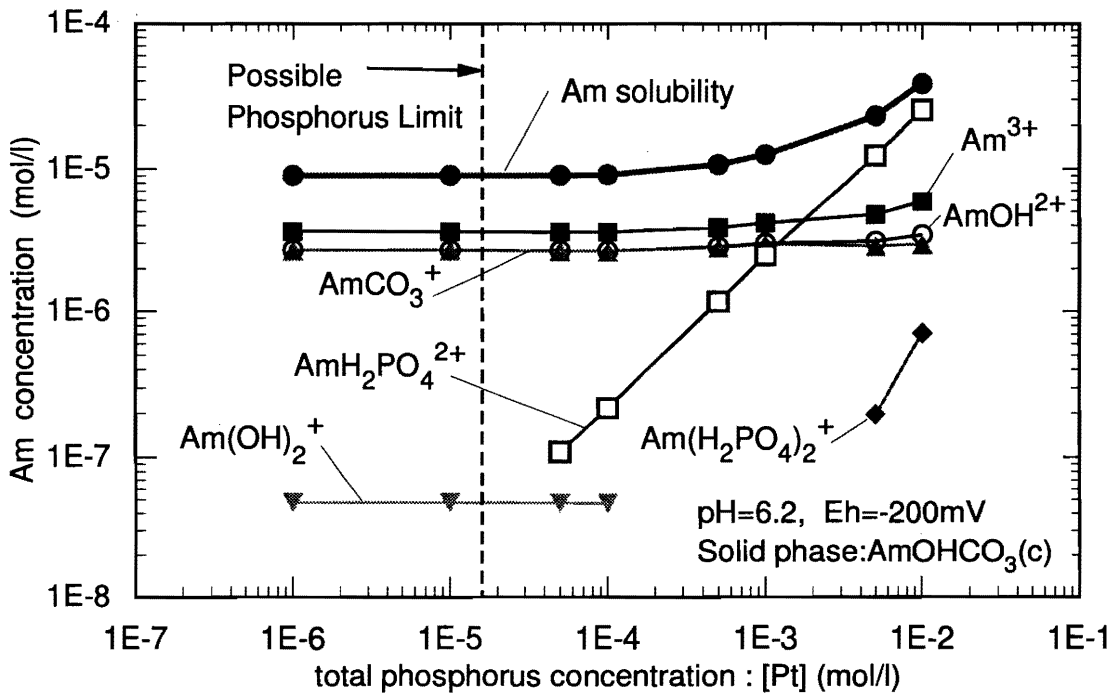Fig. 4.7 Fraction of Am(III) phosphorus complexes under pH conditions

Fig. 4.8 Effect of phosphorus concentration on americium solubility and speciation

phosphorus concentration in groundwater is more than 1×10^{-3} mol/l, the americium solubility is especially controlled by the formation of $AmH_2PO_4^{2+}$. The formation of $Am(H_2PO_4)_n^{3-n}(n=2, 3)$ besides $AmH_2PO_4^{2+}$ is not recognized in this range of phosphorus concentration.

The possible phosphorus concentration, which is estimated from the investigated chemical composition data, is in the range of 1×10^{-10} to 1.6×10^{-5} mol/l and is very low level. No americium (III) phosphorus complexes is supposed be formed, based on the calculation in this possible range of phosphorus concentration. It is suggested that there is no possibility that phosphorus concentration in groundwater has an effect on americium solubility.

4. 3. 3   Effect of F⁻ concentration (case H)

For americium(III) fluoride complexes, the existence of $AmF_n^{3-n}(n=1, 2)$ has been proven by experimental studies, and there are reliable thermodynamic data for $AmF_n^{3-n}(n=1, 2)$. The groundwater of case H shown in Table 2.6 is used to estimate the influence of fluoride concentration. Several Eh-pH conditions in case H are established in the range of pH6.0 to 8.0 and of Eh-200 to -50mV. The fluoride concentration in case H is assumed to vary from 1×10^{-6} to 1×10^{-2} mol/l. The total fraction for americium(III) fluoride complexes at Eh-200mV is shown in Fig. 4.9. The formation of $AmF_n^{3-n}(n=1, 2)$ can be confirmed in the pH range of 6.0 to 8.0. The existence of $AmF_n^{3-n}(n=1, 2)$ accounts for over 90% at pH6.2. The lower the pH value is, the higher the ratio of $AmF_n^{3-n}(n=1, 2)$ is. Fluoride concentration strikingly has an effect on americium solubility under the low pH condition. This trend for fluoride concentration is also recognized at other Eh conditions of up to -50mV. Figure 4.10 shows the result of the solubility and speciation analysis at pH6.2, which indicates the highest fraction of $AmF_n^{3-n}(n=1, 2)$. The predominant aqueous species of americium vary from the cationic forms such as Am^{3+}, $AmCO_3^+$ and $AmOH^{2+}$ to $AmF_n^{3-n}(n=1, 2)$ at the fluoride concentration of $>5 \times 10^{-4}$ mol/l. The solubility of $AmOHCO_3(c)$ tends to rise because of the increasing formation ratio of $AmF_n^{3-n}(n=1, 2)$. Americium fluoride solid, $AmF_3(c)$, is more stable than $AmOHCO_3(c)$ at the fluoride concentration of $>5 \times 10^{-3}$ mol/l. The solubility of $AmF_3(c)$ decreases under the high fluoride concentration condition. The maximum ratio of $AmF_n^{3-n}(n=1, 2)$ accounts for over 90%.

The possible fluoride concentration, which is obtained from the results of groundwater investigation, ranges from 2.6×10^{-5} to 7×10^{-4} mol/l. If americium solubility is evaluated on the basis of this possible range of fluoride concentration, it is suggested that there is the possibility that AmF_2^+ is predominant at the high fluoride concentration of about 7.0×10^{-4} mol/l. Under the condition of this fluoride concentration, americium solubility is considered to increase up to 2.0×10^{-5} mol/l. Fluoride concentration in groundwater must be over 5.0×10^{-3} mol/l so that AmF_3 (c) changes to the predominant solid phase. It is supposed that the americium solubility is hardly limited by $AmF_3(c)$ in a natural groundwater, taking account of the possible range of fluoride concentration.
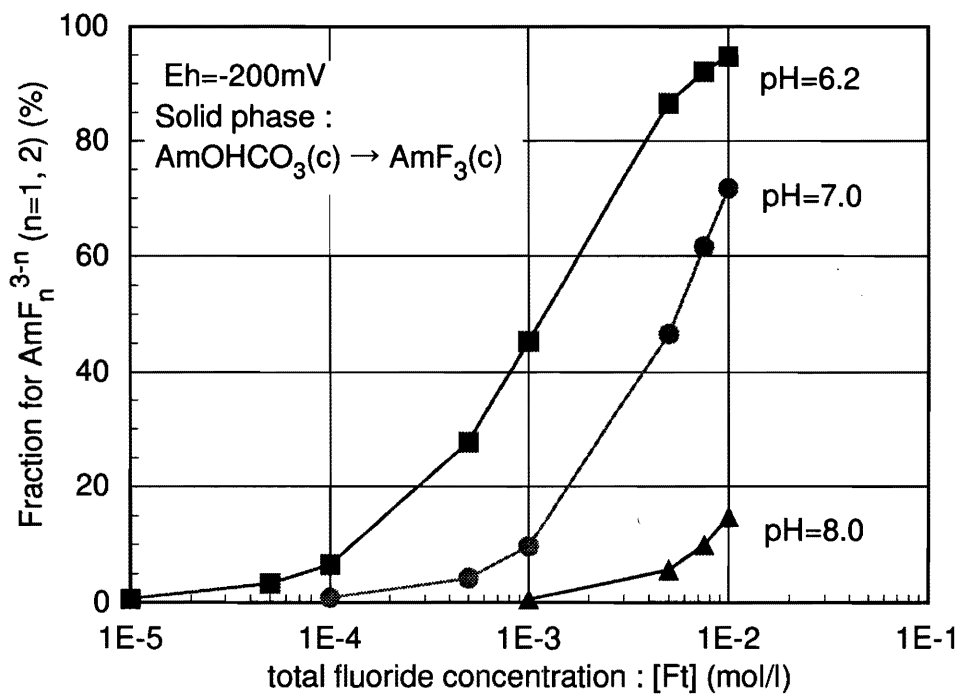
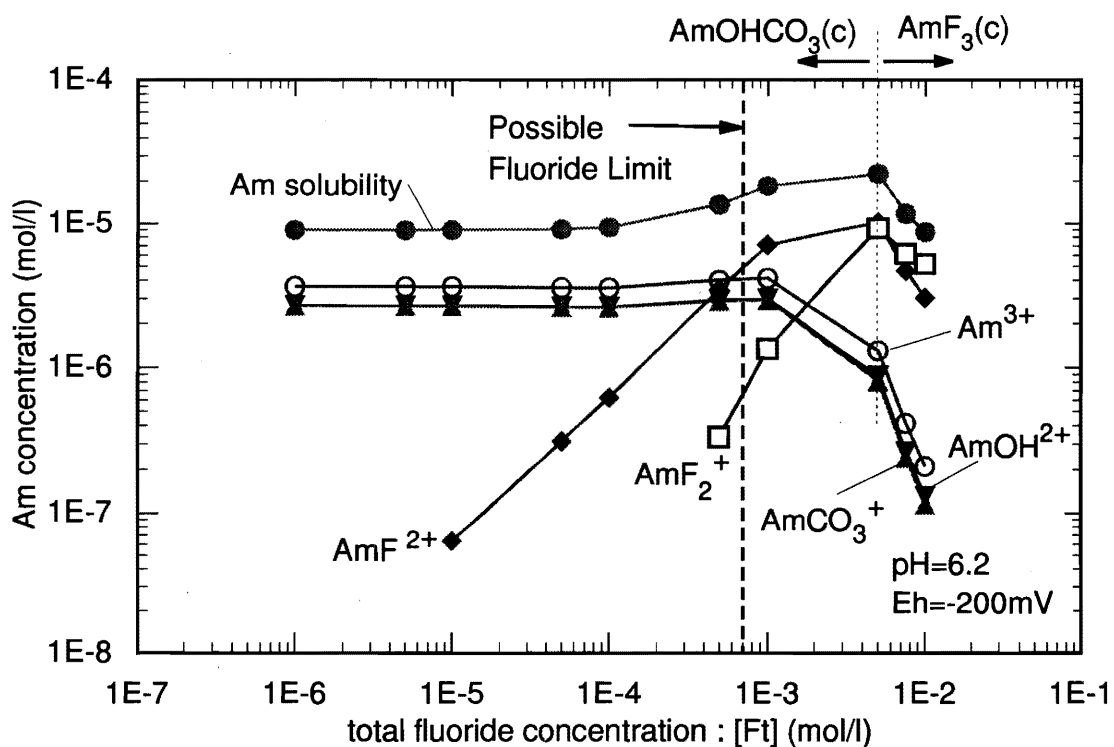Fig. 4.9 Fraction of Am(III) fluoride complexes under pH conditions

Fig. 4.10 Effect of fluoride concentration on americium solubility and speciation

4. 3. 4 Effect of SO_4^{2-} concentration (case I)

For americium sulphate complexes, the formation of $Am(SO_4)_n^{3-2n}$ (n=1 to 5) is considered in a groundwater system. The effect of sulphur concentration on americium solubility is estimated from the analyses in the saline water of case I because there is the possibility that sulphur concentration tends to be high in a saline water. Several Eh-pH conditions are assumed in the calculation of case I. The total fraction of americium(III) sulphate complexes at the high sulphur concentration of 3.0×10^{-2} mol/l is shown in Fig. 4.11. In spite of this high sulphur concentration, the formation of $Am(SO_4)_n^{3-2n}$ (n=3 to 5) can not be recognized from the calculation of case I. In the Eh range of -150 to -50mV, the fraction of $Am(SO_4)_n^{3-2n}$ (n=1, 2) increases according to decreasing pH value and accounts for over 90% at pH6.1. The formation of $Am(SO_4)_n^{3-2n}$ (n=1, 2) is especially conspicuous in the pH range of weak acidity to alkalinity. However, the fraction of americium(III) sulphate complexes decreases below pH6.5 at -200mV. Americium sulphate complexes are not dominantly formed because SO_4^{2-} is unstable under the strong reducing condition (below pH6.5 at -200mV) as mentioned on the analysis for the influence of the Eh condition (case E). The result at the condition of Eh-100mV and pH6.1, which indicates the highest ratio of $Am(SO_4)_n^{3-2n}$ (n=1, 2), is shown in Fig. 4.12. The total sulphur concentration used in calculation ranges from 1×10^{-6} to 3×10^{-2} mol/l. The americium solubility is controlled
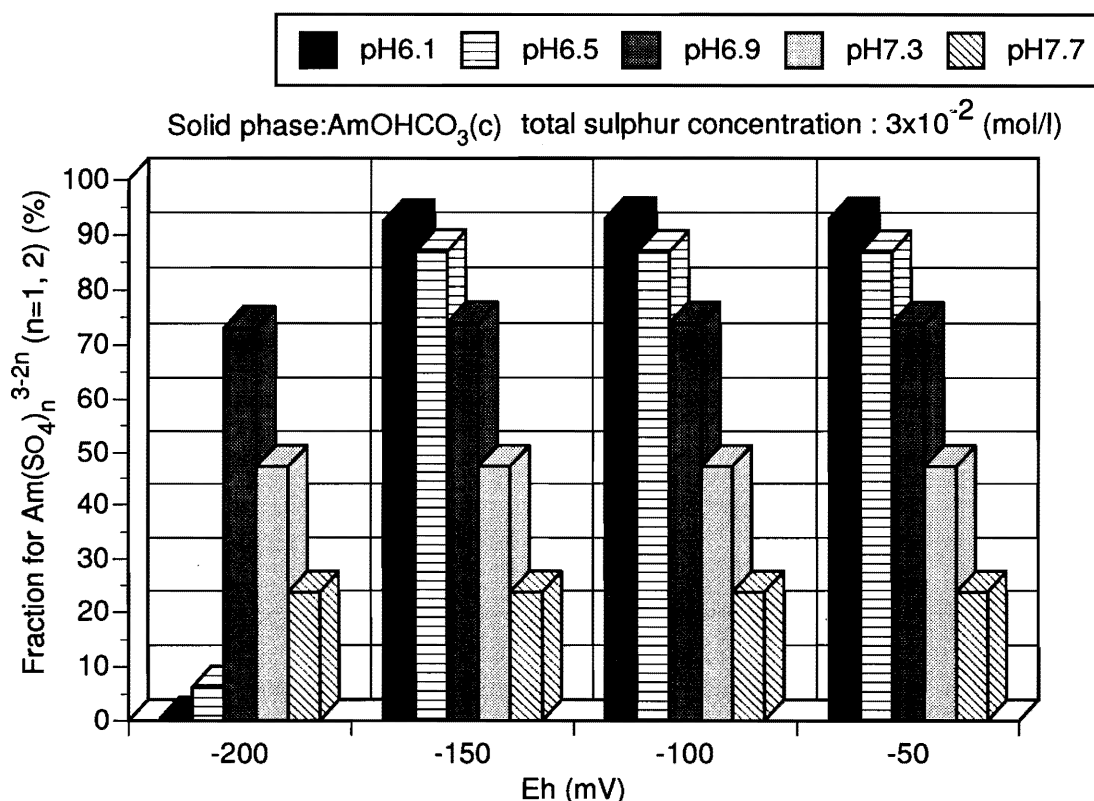

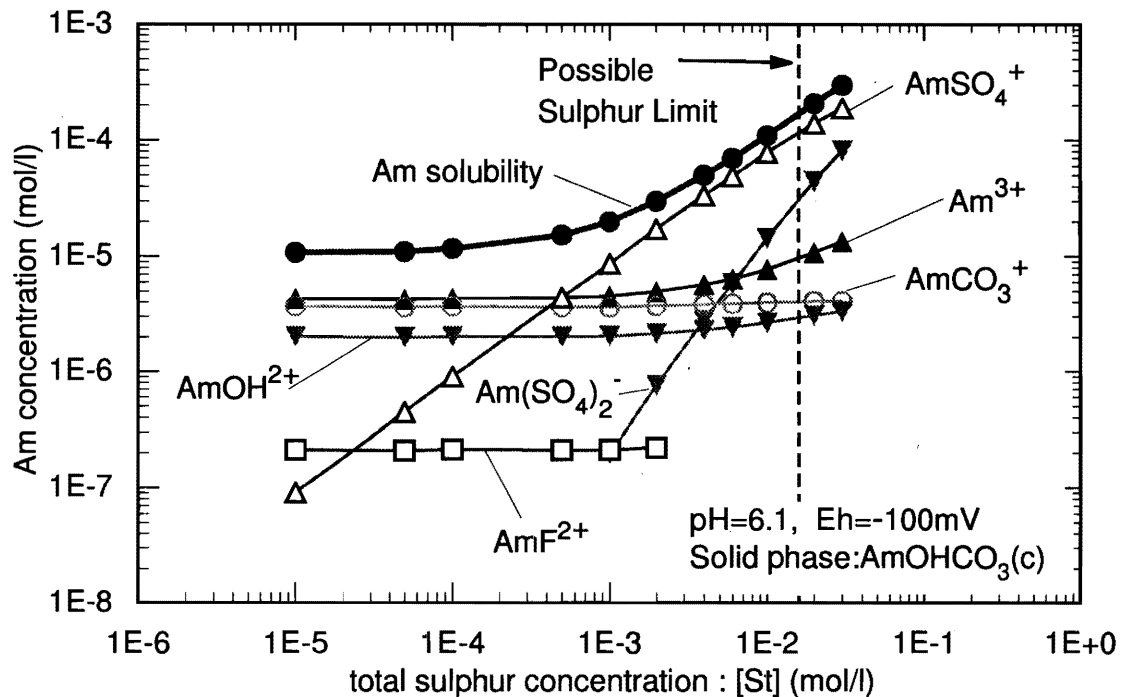Fig. 4.11 Fraction of Am(III) sulphur complexes under Eh-pH conditios

Fig. 4.12   Effect of sulphur concentration on americium solubility and speciation

by the concentration of $Am(SO_4)_n^{3-2n}$(n=1, 2), which become predominant at the sulphur concentration of >1×10^{-3} mol/l.

The sulphur concentration estimated from the investigation of chemical composition data varies from 5.2×10^{-7} to 1.6×10^{-2} mol/l. Based on this possible range of sulphur concentration, it is suggested that the dominant aqueous species changes into $Am(SO_4)_n^{3-2n}$(n=1, 2). The formation ratio of americium(III) sulphate complexes is in excess of 90% under the low pH condition. The americium solubility under the influence of sulphur concentration is estimated to increase up to 2.0×10^{-4} mol/l.

4. 3. 5   Effect of NO_3^- and NH_4^+ concentration (case J)

The JAERI data base includes the thermodynamic data of americium nitrate and ammoniate complexes, $Am(NO_3)_n^{3-n}$ (n=1 to 6) and $Am(NH_3)_n^{3+}$ (n=1 to 6). The formation of the americium ammoniate complexes is especially considered in reducing environment. The nitrogen concentration in natural groundwater is comparatively low on the basis of the investigation of chemical composition for natural groundwater. In engineered barrier, however, the nitrogen concentration may be enhanced owing to leaching $NaNO_3$(s) from bituminized waste matrix. Figure 4.13 shows the result on pH dependence, calculated in case J at Eh-200mV and total nitrogen concentration of 5×10^{-2} mol/l. The various carbon concentration is assumed in calculation to research the competition on the complexation with carbon and nitrogen. The formation ratio of $Am(NH_3)_n^{3+}$ (n=1 to 6) tends to be high at low carbon concentration in the pH range of 8 to
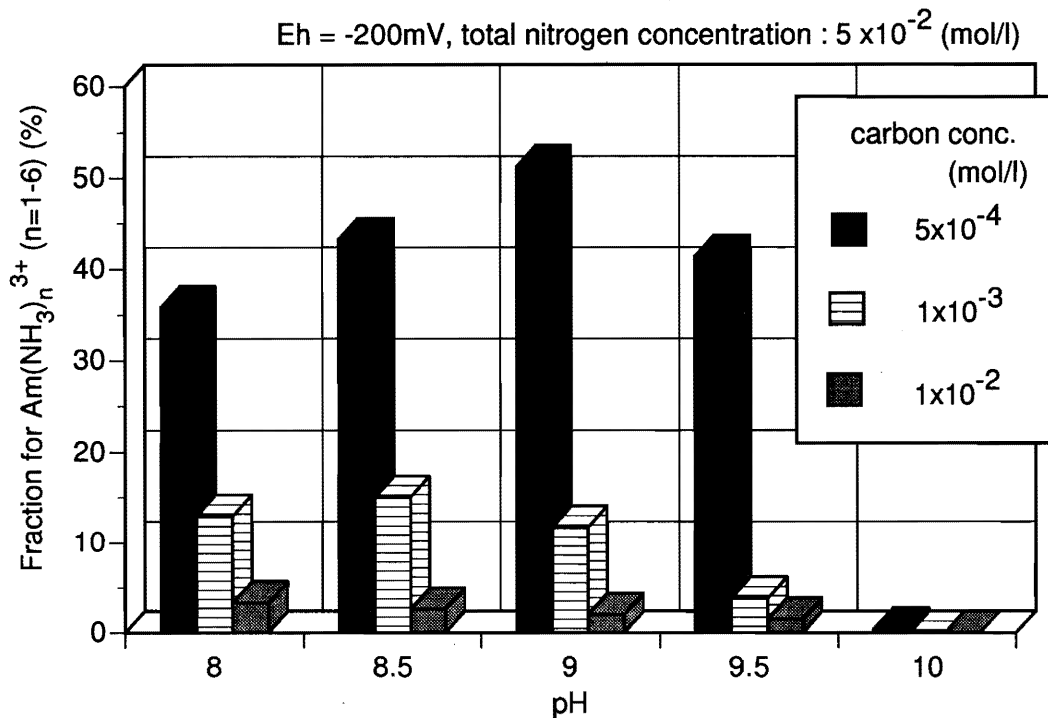
Fig. 4.13   Fraction of Am(III) ammoniate complexes depending pH condition and carbon concentration

9.5. The ratio decreases under the condition of high carbon concentration owing to the stronger complexation with carbonate than with ammoniate. The maximum ratio approximately amounted to 50% at pH9.0 and total carbon concentration of 5×10^{-4} mol/l. From the calculation assuming various Eh conditions, there is no effect of Eh value on the formation of $Am(NH_3)_n^{3+}$ (n=1 to 6) in alkaline pH. No formation of americium nitrate complexes is recognized in the calculation of case J.

Figure 4.14 shows the solubility and speciation as a function of total nitrogen concentration at pH9.0, Eh-200mV and carbon concentration of 5×10^{-4} mol/l, indicating the most remarkable effect of nitrogen concentration on americium ammoniate complexes. The concentration of americium ammoniate complexes starts to rise over total nitrogen concentration of 1×10^{-2} mol/l. The dominant americium species consists of cationic species such as $Am(NH_3)_n^{3+}$ (n=3 to 6) under the influence of high ammoniate concentration. Based on the discussion on the possible range of nitrogen concentration in section 2.3, the maximum nitrogen concentration in engineered barrier is assumed to be 2×10^{-2} mol/l. When this maximum concentration is applied to the result in Fig. 4.14, it is suggested that there is little effect of nitrogen concentration on americium solubility. The thermodynamic data for $Am(NH_3)_n^{3+}$ (n=1 to 6) are estimated from model prediction by Brown, P. L. and Wanner, H. (1987)[33]. The more reliable data with a basis of experimental studies must be provided to estimate the effect of the formation of ammoniate complexes more accurately.

Fig. 4.14   Effect of nitrogen concentration on americium solubility and speciation

4. 4   Americium solubility and speciation of case A to case J

The results of americium solubility and speciation of case A to case J are summarized as follows.

● case A, case B and case C: The solubilities of $Am(OH)_3(c)$, $Am_2(CO_3)_3(c)$ and $AmOHCO_3(c)$ are calculated in three types of groundwater (case A, B and C). All values of CO_2 partial pressure calculated in each groundwater lie within the Pco_2 range in which $AmOHCO_3(c)$ is stable. It is suggested that realistic solubility of americium is controlled by $AmOHCO_3(c)$. The dominant aqueous species of americium are estimated to be $AmCO_3^+$ at neutral pH and $AmOH(CO_3)_2^{2-}$ and $Am(OH)_2CO_3^-$ at alkaline pH.

● case D (pH condition) :   With respect to americium speciation, several cationic forms such as Am^{3+}, $AmOH^{2+}$ and $AmCO_3^+$ change into americium(III) hydroxide-carbonate complexes, $Am(OH)_2CO_3^-$, with increasing pH. Americium solubility is enhanced up to about 4×10^{-5} mol/l at low pH condition but decreases with changing to high pH value. The americium solubility decreases to 2.1×10^{-10} mol/l because of the americium solid phase changing from $AmOHCO_3(c)$ to $Am(OH)_3(c)$.

● case E (Eh condition) :   There is no effect of Eh condition on americium solubility at pH6.0. However, americium solubility and speciation may vary under strong reducing condition at

pH9.0 for the reason that $CH_4(aq)$ is more stable than carbonate and bicarbonate ion.

● case F (carbonate concentration) :   At total carbon concentration of 5.0×10^{-2} mol/l, americium solubility increases up to 1.7×10^{-5} mol/l at pH10 and falls down to 3×10^{-9} mol/l at pH13. This decrease of solubility in highly alkaline pH is based on the change of solid phase from $AmOHCO_3(c)$ to $Am(OH)_3(c)$. With increasing total carbon concentration of 1.6×10^{-4} to 5.0×10^{-2} mol/l, dominant aqueous species of americium changes as follows; $Am(OH)_2CO_3^- \rightarrow AmOH(CO_3)_2^{2-} \rightarrow Am(CO_3)_3^{3-}$. From the calculation under the various conditions of pH, Eh and carbon concentration, it is suggested that americium solubility is controlled by either $Am(OH)_3(c)$ or $AmOHCO_3(c)$.

● case G (phosphorus concentration) :   Americium phosphorus complexes are hardly formed in the possible range of phosphorus concentration in natural groundwater. It is considered that there is no possibility that phosphorus concentration has an effect on americium solubility.

● case H (fluoride concentration) : AmF^{2+} of 30 % exists in the possible range of fluoride concentration at low pH. Americium solubility slightly increases under the influence of the formation of AmF^{2+}.

● case I (sulphur concentration) :   In the pH range of weak acidity to alkalinity, the dominant aqueous species changes into $Am(SO_4)_n^{3-2n}(n=1, 2)$ with increasing sulphur concentration. Americium solubility increases up to 2.0×10^{-4} mol/l, which is about one order of magnitude higher than that at low sulphur concentration.

● case J (nitrogen concentration) :   The effect of ammoniate concentration is estimated under the assumption of the maximum nitrogen concentration determined from the solubility limit of $Ca(OH)_2(s)$ in cement system. The calculation suggests that there is little effect of nitrogen concentration on americium solubility within this nitrogen concentration level.

5. Plutonium Results

5. 1 Saline water (case A), fresh water (case B) and simulated bentonite water (case C)

Plutonium has the oxidation state of III or IV under reducing condition. Based on the thermodynamic data for plutonium (III) or (IV) solid phases, $PuO_2(c)$, $Pu(OH)_3(s)$, $Pu(OH)_4$ (am), $PuOHCO_3(s)$ and $Pu(OH)_2CO_3(s)$ are given as the solid phase limiting plutonium solubility in the calculation for saline water (case A), fresh water (case B) and simulated bentonite water (case C). The boundary between $Pu(OH)_4(am)$ and $Pu(OH)_3(s)$ in Eh-pH diagram, determined from their equilibrium constants, is close to the lower stability limit of water. The stable Eh-pH region of $Pu(OH)_3(s)$ hardly exist in reducing groundwater system. It is considered that there is little possibility that realistic plutonium solubility is controlled by $Pu(OH)_3(s)$. The speciation analysis for plutonium(IV) and (III) hydroxide-carbonate solids, $Pu(OH)_2CO_3(s)$ and $PuOHCO_3$ (s), have been carried out by PNC (1992)[6] and PSI (1995)[8], respectively. The thermodynamic data of $Pu(OH)_2CO_3(s)$ have been analogized from thorium(IV) [Kim, J.I. (1983)[38]] and have not been cited from experimental studies. The thermodynamic data of $PuOHCO_3(s)$ is also based on analogizing from $AmOHCO_3(s)$. The calculation of solubility for $Pu(OH)_2CO_3(s)$ and $PuOHCO_3(s)$ is excluded as there is no evidence that can prove their formation from previous experimental studies. Plutonium(IV) oxide and hydroxide, $PuO_2(c)$ and $Pu(OH)_4(am)$, are selected as the solid phase limiting plutonium solubility. The selected thermodynamic data of $PuO_2(c)$ is cited from Kim, J.I.(1989)[48]. Kim, J. I. (1989) estimated the solubility product of $PuO_2(c)$ from the measurements of solubility after three years and compared their results with several values reported previously. Kim, J. I. (1989) reported that large differences among the compared data are caused by the influence of $PuO_2 \cdot nH_2O$ formed on the surface of $PuO_2(c)$. The two solubility products of $PuO_2(c)$, one (logK=60.2) of which was obtained from the experimental work of Kim, J. I. (1989), and another (logK=63.8) of which was recalculated by Kim, J. I. (1989) from the review of some previous data, are selected here.

The results of plutonium solubility analyses in case A, B and C are given in Table 5.1. The solubilities of $PuO_2(c)$ for two logK values make a difference of 3 or 4 orders of magnitude. The solubilities of $PuO_2(c)$ are about 2 orders of magnitude lower than that of $Pu(OH)_4(am)$. The highest solubility of $Pu(OH)_4(am)$ is calculated to be 3.8×10^{-7} mol/l in case C. Taking into account the concervative solubility, the solid phase limiting plutonium solubility is adequate to be $Pu(OH)_4(am)$. The dominant aqueous species in case A are plutonium(III) cationic forms, $PuCO_3^+$ and $PuSO_4^+$. Plutonium(III) cationic forms transform into plutonium(IV) hydroxide-carbonate complex, $Pu(OH)_2(CO_3)_2^{2-}$, under the pH condition of neutrality to alkalinity. The formation ratio of $Pu(OH)_2(CO_3)_2^{2-}$ accounts for about 100% in case C.

Table 5.1 Plutonium solubilities and speciation for saline water (caseA), fresh water (case B) and simulated bentonite water (case C).

Type of water	pH Eh (mV)	solubility (mol/l)		speciation (%)	
		PuO2(c)	Pu(OH)4(am)		
Saline water (case A)	6.9 -200	3.0×10^{-10} (logK*=60.2) 7.0×10^{-14} (logK*=63.8)	6.5×10^{-8}	PuCO3+ PuSO4+ Pu(OH)2(CO3)2^{2-} Pu^{3+} Pu(SO4)2^-	69.0 16.3 9.0 4.2 1.0
Fresh water (case B)	7.4 -200	3.0×10^{-11} (logK*=60.2) 7.0×10^{-15} (logK*=63.8)	6.5×10^{-9}	Pu(OH)2(CO3)2^{2-} PuCO3+	77.5 21.7
Simulated bentonite water (case C)	8.9 -397	1.7×10^{-9} (logK*=60.2) 4.3×10^{-13} (logK*=63.8)	3.8×10^{-7}	Pu(OH)2(CO3)2^{2-}	99.9

* logK for the reaction : $Pu^{4+} + 4OH^- = PuO_2(c) + 2H_2O$

5. 2 Effect of pH and Eh conditions (case D and case E)

The pH dependence of plutonium solubility is estimated from the analyses for the groundwater of case D, assuming the constant Eh (-200mV) and the pH range of 6.0 to 13.0. The result in case D is given in Fig. 5.1. According to the pH change, the dominant plutonium species are divided into three groups as shown in Fig. 5.1. The dominant species are estimated to be cationic forms of plutonium(III) under the pH condition of 6.0 to 7.0. In the pH range of 7.0 to 11.5, they change into plutonium(IV) hydroxide-carbonate complex, $Pu(OH)_2(CO_3)_2^{2-}$. Over pH11.5, the major aqueous species consists of $Pu(OH)_4(CO_3)_2^{4-}$. The solubility profile depends on the concentration of these dominant species in each pH region. Although the dominant aqueous forms have the oxidation state of III at weak acid pH, the stable solid phase of plutonium is estimated to be in the state of IV. The solubility of $Pu(OH)_4(am)$ basically decreases with increasing pH. The maximum plutonium solubility at pH6.0 is approximately calculated to be 8.0×10^{-6} mol/l.

In order to investigate the effect of Eh condition in the acid and alkaline groundwater of case E, various Eh values are assumed at two pH conditions, pH6.0 and pH9.0. The plutonium solubility at pH6.0 is shown in Fig. 5.2. The Eh value ranges from -200 to +200mV. Based on the discussion on the solid phase limiting plutonium solubility in section 5. 1, plutonium solubility is assumed to be controlled by $Pu(OH)_4(am)$. With respect to the dominant aqueous species,
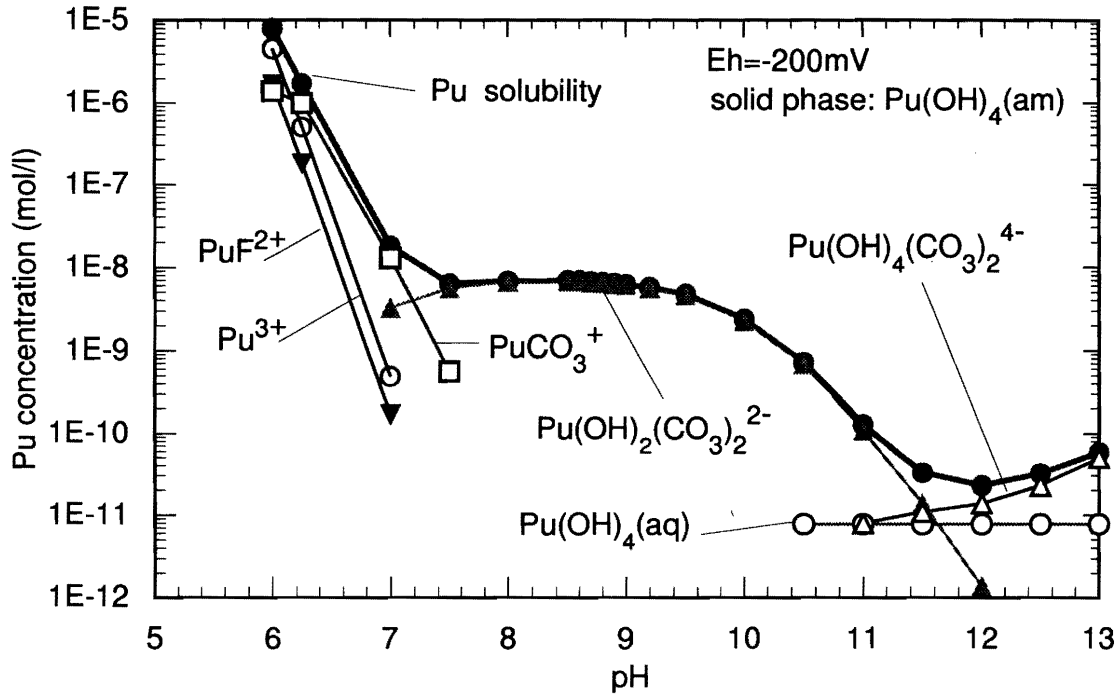
Fig. 5.1 Plutonium solubility and speciation for the groundwater (case D) assuming the constant Eh (-200mV) and the pH range of 6.0 to 13.0
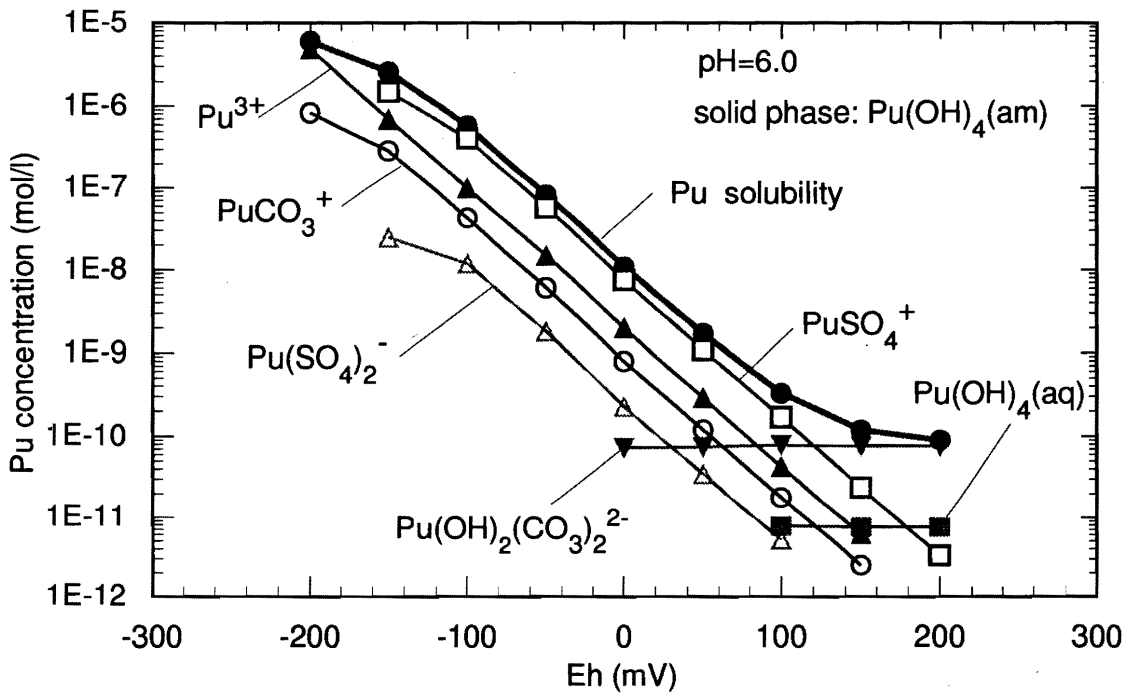

Fig. 5.2 Plutonium solubility and speciation for the groundwater (case E) assuming the constant pH6.0 and the Eh range of -200 to +200mV.
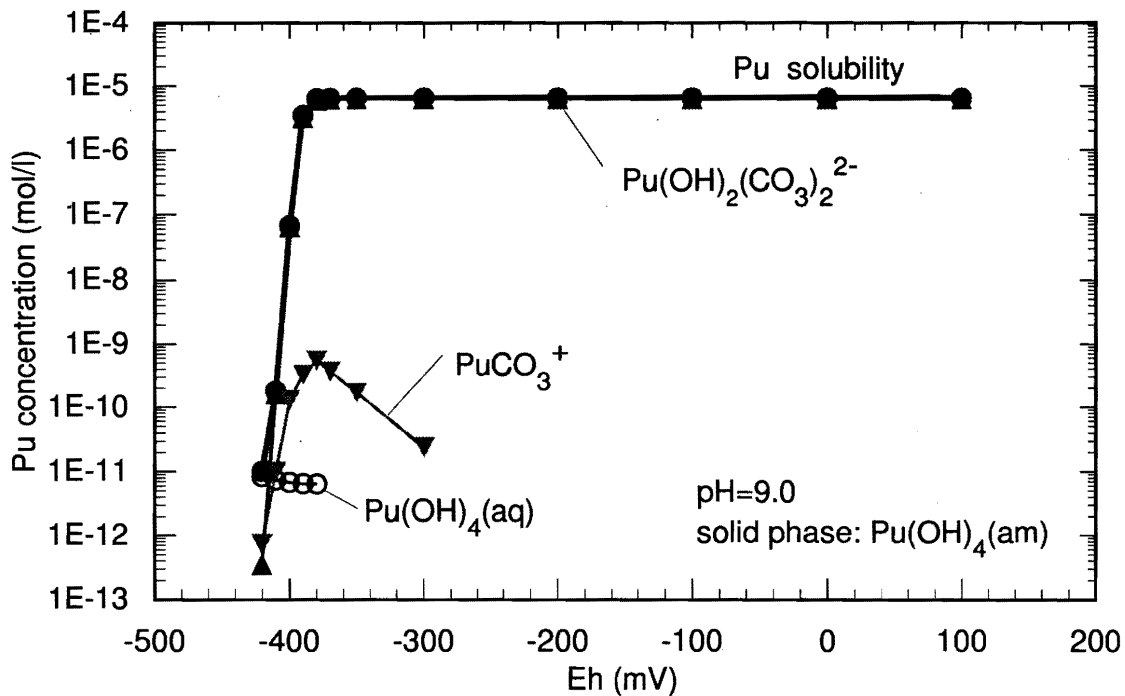
Fig. 5.3 Plutonium solubility and speciation for the groundwater (case E) assuming the constant pH9.0 and the Eh range of -400 to +100mV.

plutonium(III) cationic forms such as Pu^{3+}, $PuSO_4^+$ and $PuCO_3^+$ are stable under the Eh condition of -200 to +150 mV. The dominant species change into plutonium(IV) hydroxide-carbonate complex, $Pu(OH)_2(CO_3)_2^{2-}$, over Eh+150mV. The solubility of $Pu(OH)_4(am)$ rises with increasing Eh value. The highest plutonium solubility, about 6.0×10^{-6} mol/l, is calculated at pH6.0 and Eh-200mV. The plutonium solubility at pH6.0 indicates the change of about five orders of magnitude owing to the Eh variation. It is suggested that the Eh condition has an effect on the plutonium solubility at weak acid pH.

Figure 5.3 shows the plutonium solubility influenced by the Eh condition at pH9.0. The effect of Eh parameter on plutonium solubility appears at the strong reducing condition of about -400mV. At about -400mV, plutonium solubility remarkably increases up to 6.5×10^{-6} mol/l as shown in Fig. 5.3 . This change of the plutonium solubility under about -400mV is controlled by the change of dominant carbon species. $CH_4(aq)$ is more stable than CO_3^{2-} or HCO_3^- under the Eh condition of < -400mV at pH9.0, so that plutonium(IV) carbonate complexes are not dominantly created under this strong Eh condition. The superior formation of plutonium(IV) carbonate complexes under the Eh condition of > -400mV leads to the increase of plutonium solubility. In the Eh range of -380 to +100mV, the solubility is constant and not dependent on the Eh condition. The dominant aqueous species is estimated to be $Pu(OH)_2(CO_3)_2^{2-}$, at the Eh condition of > -400mV. No existence of the chemical forms of plutonium(V) or (VI) is recognized from the calculation under the various Eh condition at pH6.0 and pH9.0. From the results in case E, the plutonium solubility within the Eh-pH condition under which plutonium(III) aqueous

species is dominant strongly depends on Eh parameter. In the case that plutonium(IV) aqueous species predominantly formed, plutonium solubility is hardly effected by Eh condition besides low Eh condition under which the formation of plutonium(IV) hydroxide-carbonate complexes is inhibited.

5. 3   Effect of various ligand concentration

5. 3. 1   Effect of CO_3^{2-} concentration (case F)

Two kinds of data set on plutonium(IV) hydroxide-carbonate complexes are assumed in the calculation owing to the uncertainty of the formation of hydroxide-carbonate complexes as mentioned in section 3. The formation of $Pu(OH)_n(CO_3)_2^{n-}$ (n=2,4) according to Yamaguchi, T. (1994)[40] and $Pu(OH)_nCO_3^{2-n}$ (n=3,4) according to Eriksen,T. E. (1993)[43], is considered in data set A and data set B, respectively. The effect of carbon concentration on plutonium solubility is estimated from the calculation for the groundwater of case F assuming various total carbon concentration. The Eh-pH dependance for the complexation of carbon is also investigated in this calculation. Figure 5. 4 shows the result in case F analyzed at Eh-200mV and total carbon concentration of 5×10^{-2} mol/l using data set A. This result can be compared with the calculation for pH parameter in case D. The solubility profile in case F is similar to that in case D. Both the solubilities are controlled by the formation of hydroxide-carbonate complexes, $Pu(OH)_n(CO_3)_2^{n-}$ (n=2,4). The solubility at weak alkaline pH ($8 < pH < 9$) is about two orders of magnitude higher than that at strong pH ($> pH11$) at total carbon concentration of 5×10^{-2} mol/l. Owing to the higher carbon concentration in case F, the plutonium solubility in case F is about three orders of magnitude higher than that in case D. The effect of Eh change of -400 to -100mV is also examined. However, there is no effect of Eh value on the solubility curve at the pH range of 8.0 to 13.0.

Figure 5.5 shows the plutonium solubility and speciation at pH9.0 as a function of total carbon concentration, based on data set A. The range of the carbon concentration used here is from 1×10^{-4} to 5×10^{-2} mol/l. In this carbon concentration range, a major aqueous species is plutonium(IV) hydroxide-carbonate complex, $Pu(OH)_2(CO_3)_2^{2-}$. The solubility of $Pu(OH)_4$(am) depends on the formation of $Pu(OH)_2(CO_3)_2^{2-}$. The solubility increases up to about 6.5×10^{-5} mol/l and is 5 orders of magnitude higher than that at the low carbon concentration of 1×10^{-4} mol/l. Figure 5. 6 shows the result calculated using data set B. The solubility increases at carbon concentration of $> 1 \times 10^{-3}$ mol/l owing to the formation of $Pu(OH)_nCO_3^{2-n}$ (n=3,4). The solubility amounts to 2.0×10^{-10} mol/l at carbon concentration of 5×10^{-2} mol/l. The comparison of the plutonium solubilities calculated using data set A and B is shown in Fig. 5.7. The measured solubility data in the pH range of 9.0 to 11.5, according to Lierse, CH. (1986)[39] and Yamaguchi, T. (1994)[40], are also plotted in Fig. 5.7. Two solubilities were measured as a function of carbon
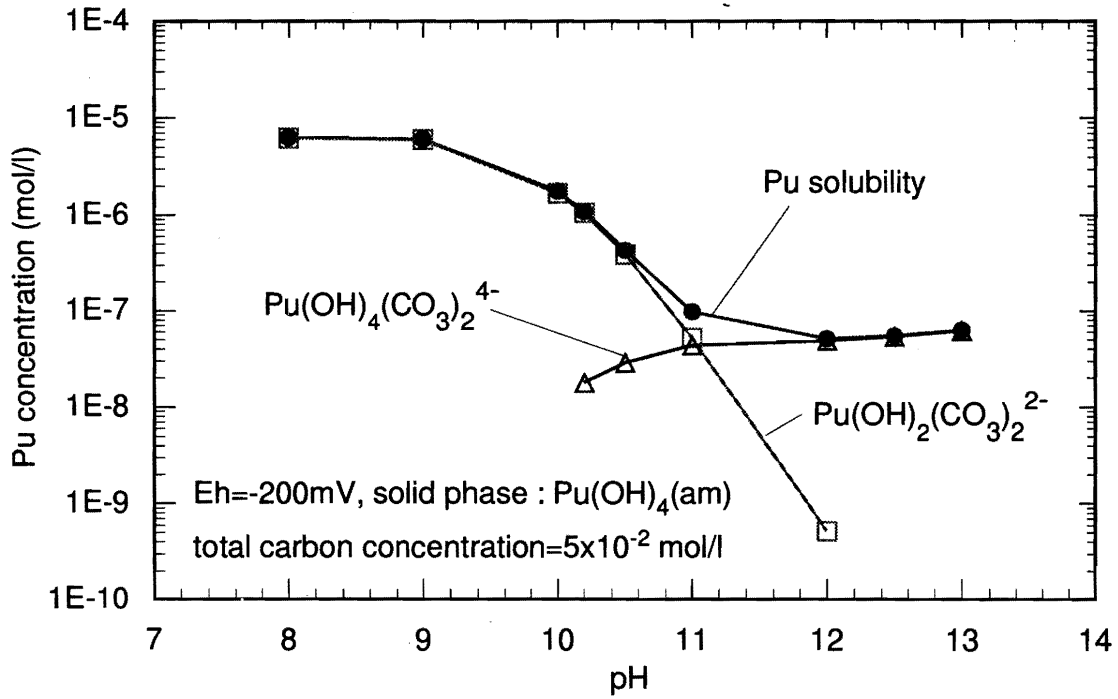
Fig. 5.4   pH dependance of plutonium solubility at Eh-200mV and total carbon concentration of 5×10^{-2} mol/l

Fig. 5.5   Effect of carbonate concentration on Pu solubility and speciation estimated using thermodynamic data of $Pu(OH)_n(CO_3)_2{}^{n-}$ (n=2,4) (Yamaguchi, T.,1994)[38]
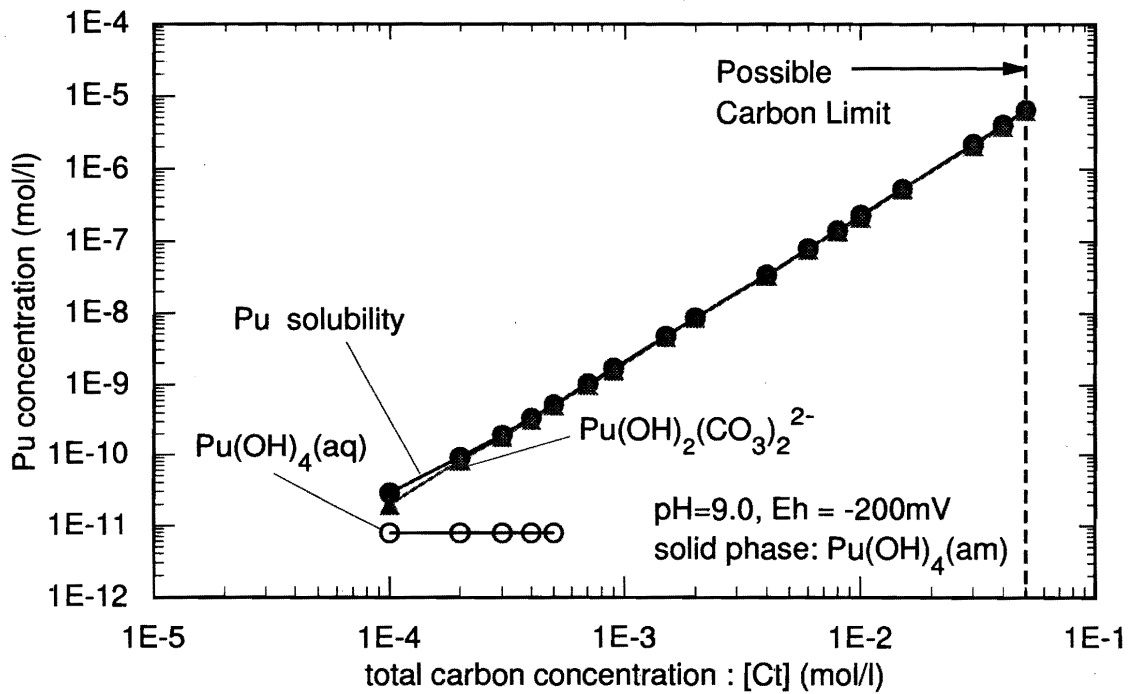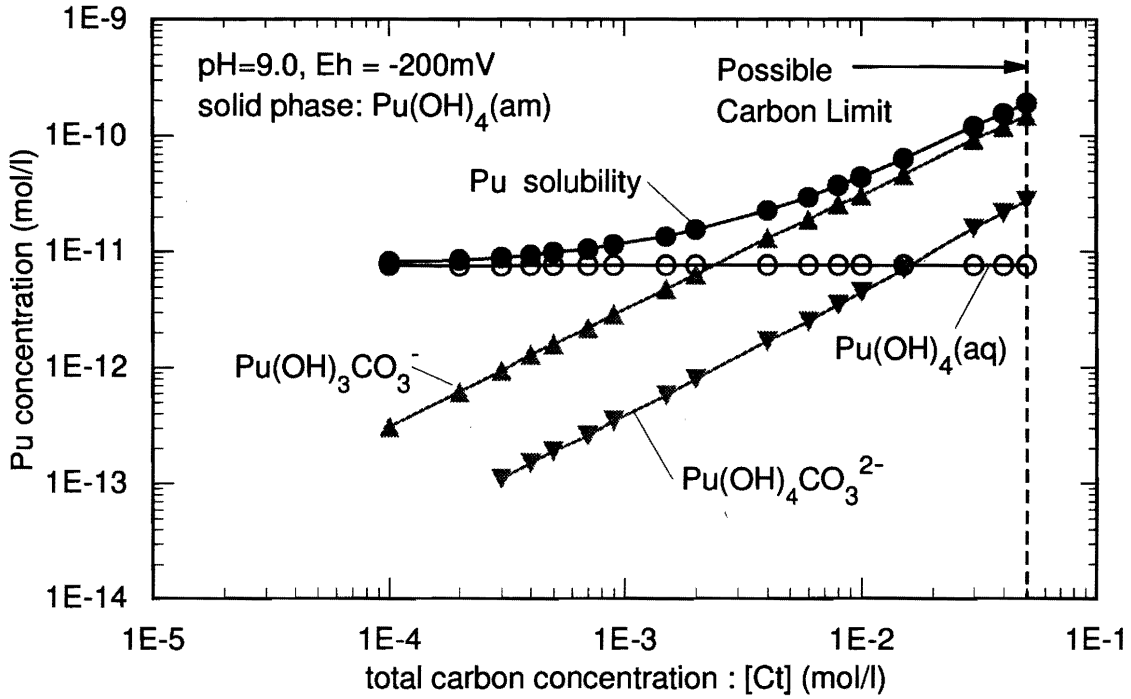
Fig. 5.6 Effect of carbonate concentration on Pu solubility and speciation estimated using thermodynamic data of $Pu(OH)_nCO_3^{2-n}(n=3,4)$ (Eriksen,T.E.,1993)[43]
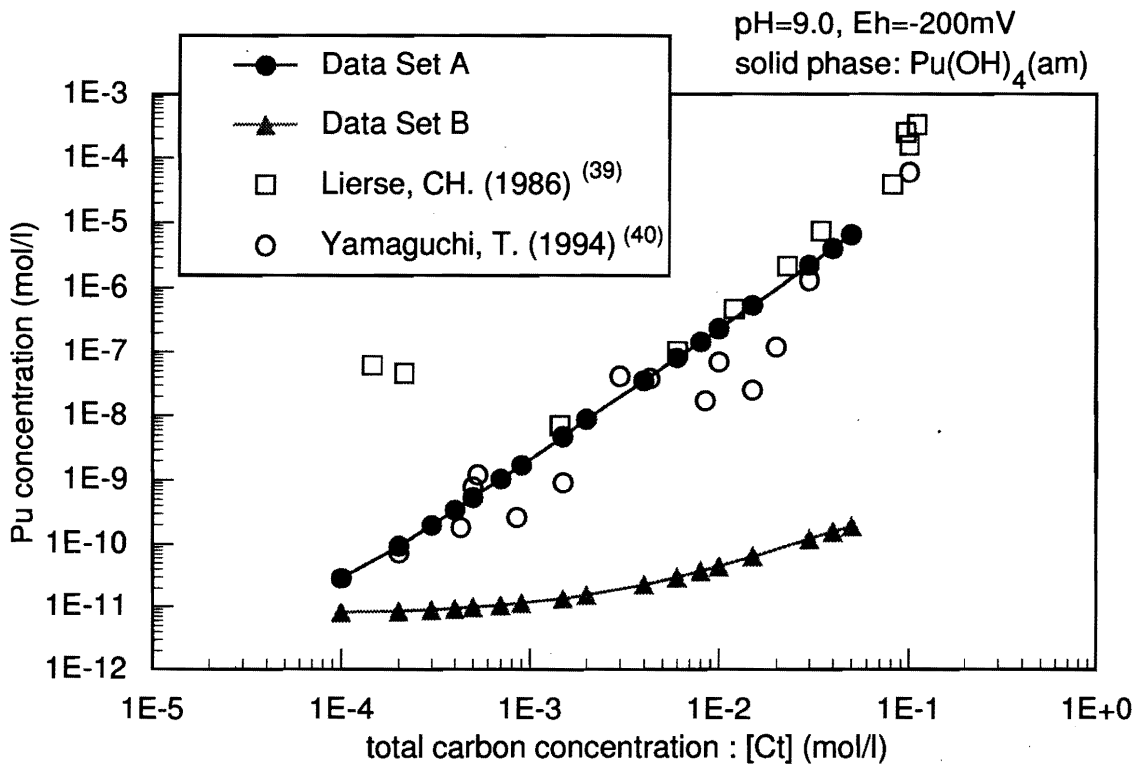

Fig. 5.7 Comparison of plutonium solubilities between the calculations from data set A and B and the measurments according to Lierse, CH. (1986)[39] and Yamaguchi, T. (1994)[40]

concentration. The increasing trend of measured plutonium solubility owing to high carbon concentration is in good agreement with the result calculated using data set A. Based on the comparison between calculation and measurement, it is suggested that the thermodynamic data of plutonium(IV) hydroxide-carbonate complex in data set A is more reliable than those in data set B. Data set A has been used in all the calculations except for case F.

The maximum carbon concentration in solution, discussed in section 2.3, is approximately 5×10^{-2} mol/l. If this carbon concentration limit is allowed in groundwater, the plutonium solubility increases up to about 6.5×10^{-5} mol/l with increasing carbonate concentration. Taking account of the possible range of carbon concentration shown in Table 2.6, the dominant plutonium species in alkaline groundwater are estimated to be $Pu(OH)_n(CO_3)_2^{n-}$ (n=2,4).

5. 3. 2 Effect of PO_4^{3-} concentration (case G)

With respect to the phosphorus complexes of plutonium, the thermodynamic data for both $Pu(H_2PO_4)_n^{3-n}$ (n=1, 2) of plutonium(III) and $Pu(H_2PO_4)_n^{4-n}$ (n=1, 2, 4) of plutonium(IV) are considered in the JAERI data base. The formation of $Pu(HPO_4)_n^{4-2n}$ (n=1-4) has been estimated from the experimental study of Denotkina, R. G.(1960)[49]. His data are referred in data base of Puigdomenech, I. (1991)[35]. However, Cowan, C. E. (1985)[50] and the IAEA (1992)[37] have judged it difficult to prove the complexation of plutonium(IV) with HPO_4^{2-} with the basis of experimental results of Denotkina, R. G. (1960). They have removed the $Pu(HPO_4)_n^{4-2n}$ (n=1-4)
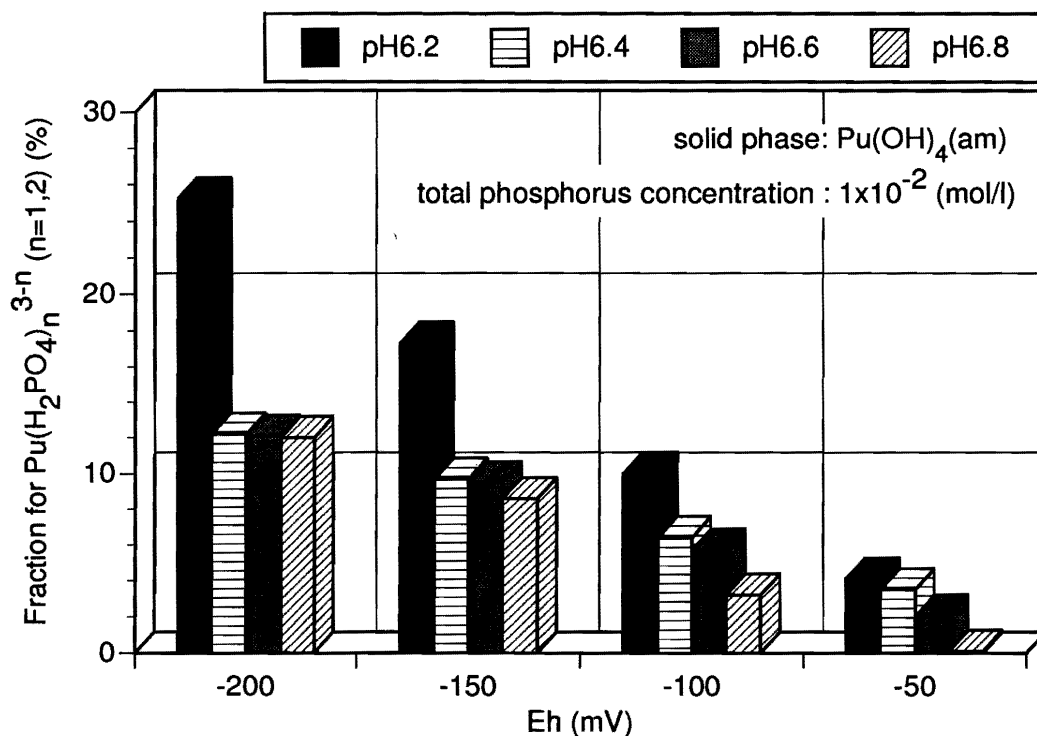

Fig. 5.8 Fraction of Pu(III) phosphorus complexes at several Eh-pH conditions

data in their data bases. In this study, the $Pu(HPO_4)_n^{4-2n}$ (n=1-4) data are treated as the auxiliary data. The thermodynamic data on the plutonium phosphorus complexes are considered as the following data set A and B.

— data set A : $Pu(H_2PO_4)_n^{3-n}$ (n=1, 2) and $Pu(H_2PO_4)_n^{4-n}$ (n=1, 2, 4)
— data set B : $Pu(H_2PO_4)_n^{3-n}$ (n=1, 2), $Pu(H_2PO_4)_n^{4-n}$ (n=1, 2, 4) and $Pu(HPO_4)_n^{4-2n}$ (n=1-4)

The effect of the phosphorus concentration on plutonium solubility is estimated from the analyses for the groundwater of case G assuming the various phosphorus concentration. Plutonium solubilities in case G are calculated in the Eh range of -200 to -50mV and pH range of 6.0 to 8.0. Figure 5.8 shows the fraction of plutonium phosphorus complexes at the phosphorus concentration of 1×10^{-2}mol/l. The data set A is used in analyses. Plutonium(III) phosphorus complexes, Pu $(H_2PO_4)_n^{3-n}$ (n=1, 2), are dominantly created, however, the formation of plutonium(IV) phosphorus complexes, $Pu(H_2PO_4)_n^{4-n}$ (n=1, 2, 4), is not recognized under these chemical compositions. The fraction of plutonium(III) phosphorus complexes tends to increase under low Eh-pH condition. The maximum fraction of plutonium phosphorus complexes accounts for about 25% at Eh-200mV and pH6.2. The solubility and speciation at Eh-200mV and pH<6.2, which is the most remarkably influenced by phosphorus concentration, are shown in Fig. 5.9. The solubility of
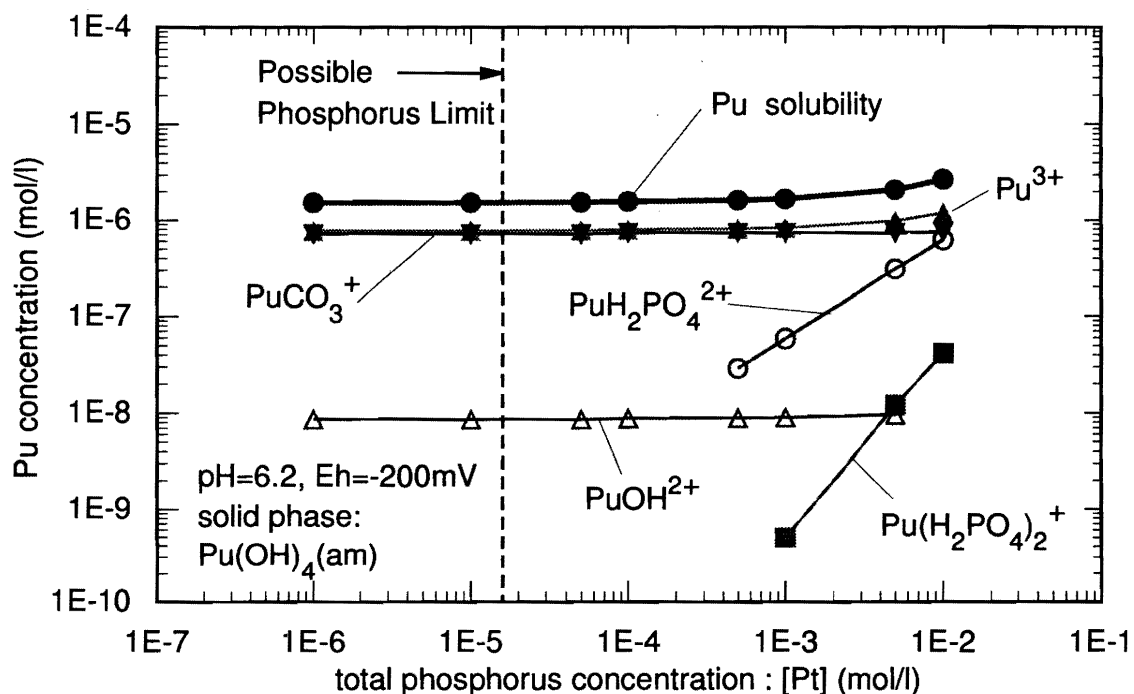

Fig. 5.9 Effect of phosphorus concentration on Pu solubility and speciation calculated using the thermodynamic data set A, $Pu(H_2PO_4)_n^{3-n}$ (n=1, 2) and $Pu(H_2PO_4)_n^{4-n}$ (n=1, 2, 4).
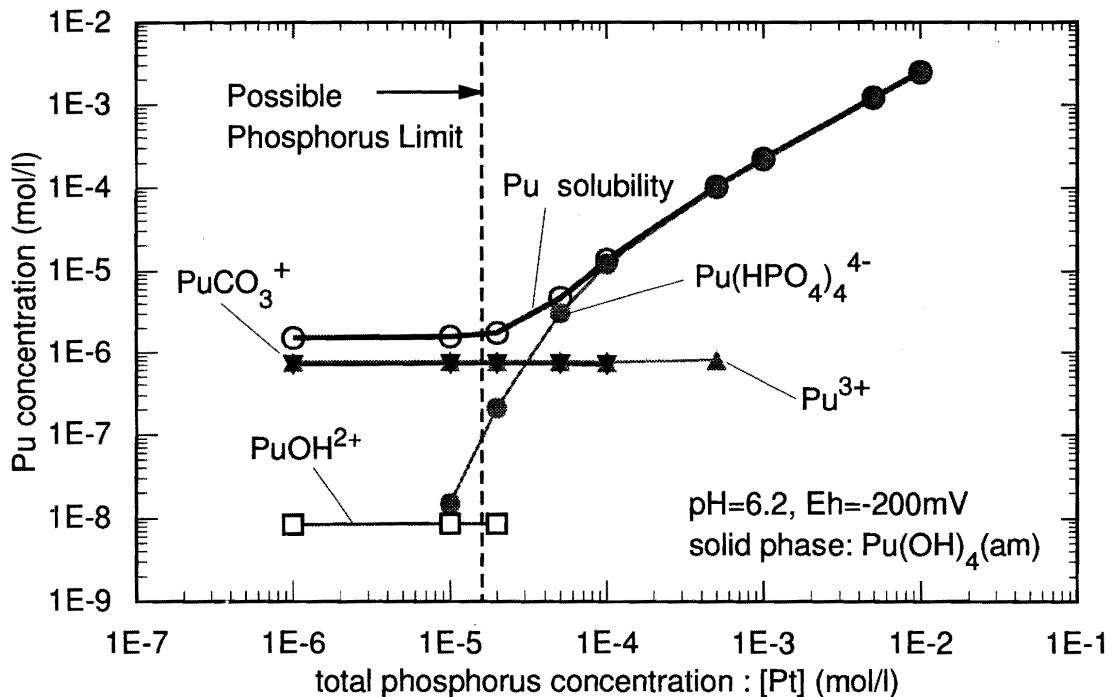
Fig. 5.10 Effect of phosphorus concentration on Pu solubility and speciation calculated using the thermodynamic data set B, $Pu(H_2PO_4)_n^{3-n}$ (n=1, 2), $Pu(H_2PO_4)_n^{4-n}$(n=1, 2, 4) and $Pu(HPO_4)_n^{4-2n}$(n=1-4)

$Pu(OH)_4$(am) slightly increases at the phosphorus concentration of $> 1\times10^{-3}$ mol/l owing to the formation of $Pu(H_2PO_4)_n^{3-n}$(n=1, 2). The concentration of Pu^{3+} or $PuCO_3^+$ as the dominant aqueous species is higher than that of $PuH_2PO_4^{2+}$ in the range of the phosphorus concentration of 10^{-6} to 10^{-2}mol/l. The result for the data set B assuming the existence of $Pu(HPO_4)_n^{4-2n}$(n=1-4) is given in Fig. 5.10. If the thermodynamic data of $Pu(HPO_4)_n^{4-2n}$(n=1-4) is also considered in this data base, the solubility of $Pu(OH)_4$(am) strongly depends on the phosphorus concentration of $> 2\times10^{-5}$mol/l as shown in Fig. 5.10. The formation of $Pu(HPO_4)_4^{4-}$ with increasing phosphorus concentration has an effect on plutonium solubility.

The range of the phosphorus concentration, which is estimated from the chemical composition data survey, is from 1.0×10^{-10} to 1.6×10^{-5} mol/l in Table 2.6. $Pu(HPO_4)_4^{4-}$ of about 12% may exist at phosphorus concentration of 2×10^{-5} mol/l. If the results in case G are estimated in this range, plutonium(IV) phosphorus complexes are hardly created for both calculations shown in Fig. 5.9 and Fig. 5.10.

5. 3. 3 Effect of F⁻ concentration (case H)

Plutonium fluoride complexes formed under a reducing condition are considered to be PuF_n^{3-n} (n=1, 2) of plutonium(III) and PuF_n^{4-n} (n=1,2) of plutonium(IV). The thermodynamic
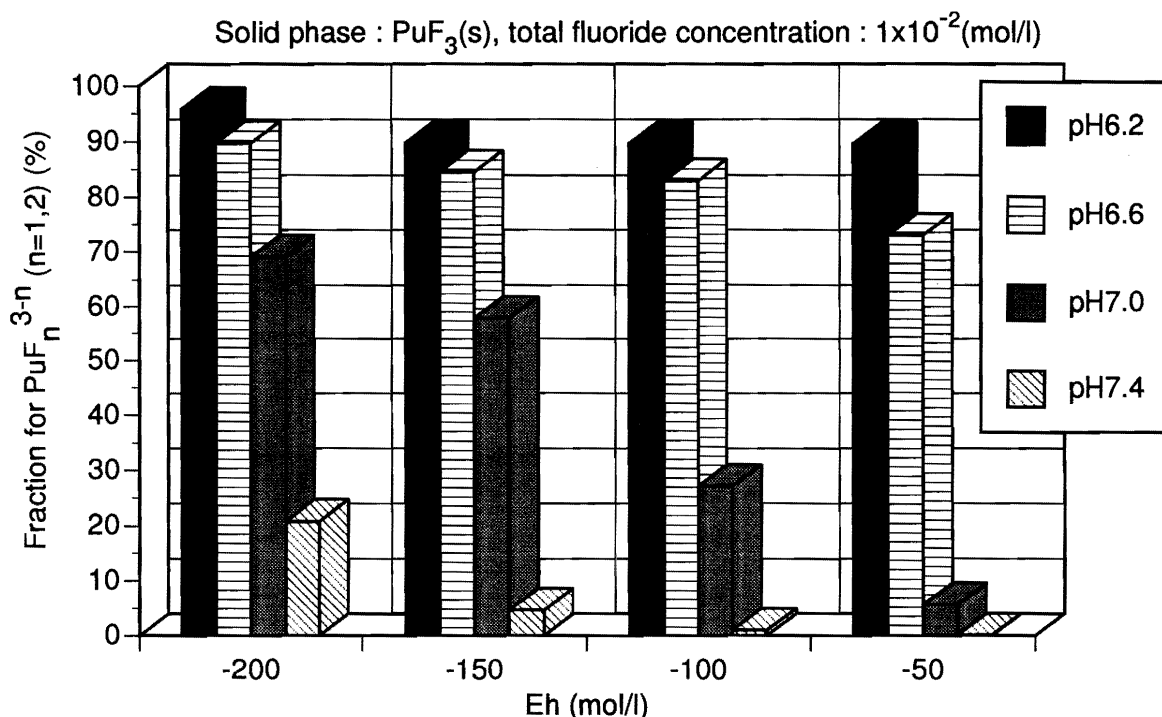
Solid phase : $PuF_3(s)$, total fluoride concentration : $1 \times 10^{-2}(mol/l)$

Fig. 5.11 Fraction of Pu(III) fluoride complexes at several Eh-pH conditions

data of PuF_n^{3-n} (n=1, 2) have been reported by the model prediction and hardly estimated from an experiment. The data of PuF_n^{3-n} (n=1, 2) analogized from the data of americium(III) fluoride complexes were selected in the data base indicated by Nitsche, H.(1991)[34]. In order to investigate the influence of fluoride concentration on the plutonium solubility, the data of both PuF_n^{3-n}(n=1, 2) and PuF_n^{4-n}(n=1,2) are considered in this data base. The groundwater (case H) assuming that the fluoride concentration ranges from 10^{-6} to 10^{-2}mol/l is used in this analysis. Several Eh-pH conditions are assumed to be in the Eh range of -200 to -50mV and the pH range of 6.0 to 8.0. The fraction of plutonium fluoride complexes at the fluoride concentration of 10^{-2}mol/l is indicated in Fig. 5.11. The fraction of PuF_n^{3-n} (n=1, 2) seems to increase at low pH and accounts for over 50% at pH6.2 in the Eh range of -200 to -50mV. The fraction of PuF_n^{3-n} (n=1, 2) also tends to become high with decreasing Eh. No formation of PuF_n^{4-n}(n=1,2) is confirmed under this Eh-pH condition. The solubility and speciation analyzed at pH6.2 and Eh-200mV, showing the most conspicuous effect of fluoride concentration, are given in Fig. 5.12. The concentration of PuF^{2+} increases at the fluoride concentration of $> 10^{-5}$mol/l, but this increase negligibly enhances the solubility. $Pu(OH)_4(am)$ restricting the plutonium solubility changes into $PuF_3(s)$ at the fluoride concentration of $> 5 \times 10^{-5}$mol/l, so that the plutonium solubility decreases with increasing fluoride concentration. The predominant aqueous species is PuF^{2+} under the condition of the fluoride concentration at which $PuF_3(s)$ is stable,

As shown in Table 2.6, the possible range of the fluoride concentration, determined from the investigated chemical composition data, is from 2.6×10^{-5} to 7.0×10^{-4} mol/l. Taking into
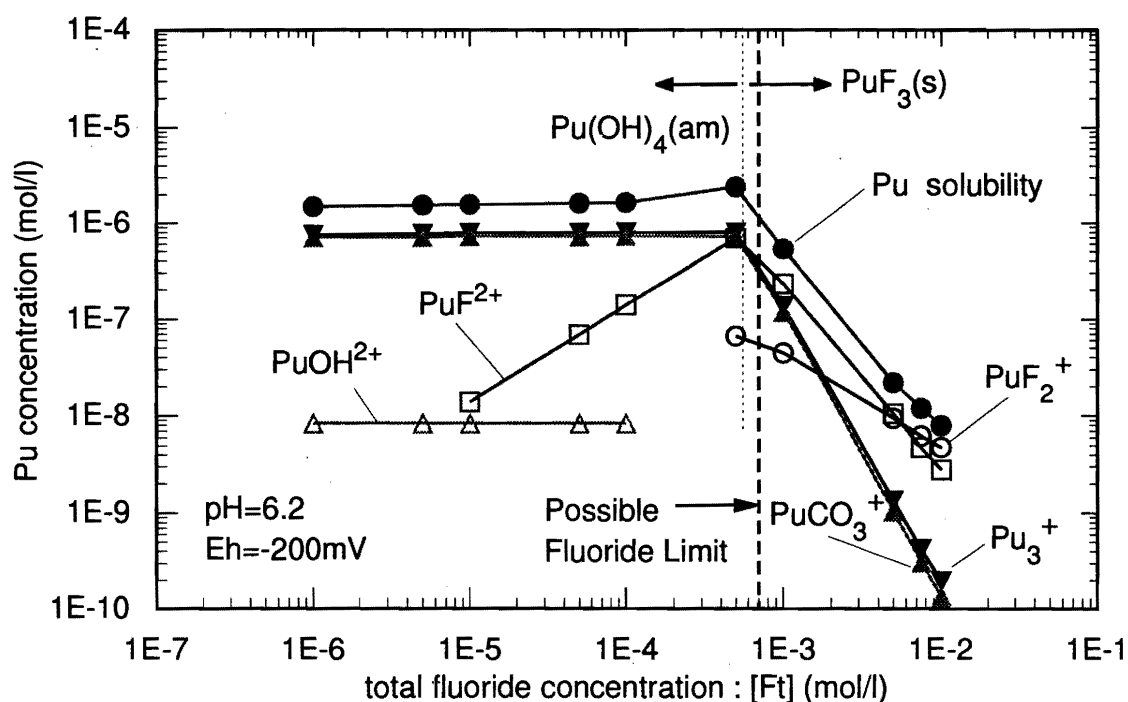
Fig. 5.12   Effect of fluoride concentration on plutonium solubility and speciation

account this range of the fluoride concentration, if a natural groundwater contain fluoride ion of about 7.0×10^{-4} mol/l, plutonium aqueous phase consists of PuF^{2+} over 30%. The solubility slightly changes from 1.6×10^{-6} to 2.4×10^{-6} mol/l with increasing fluoride concentration. It is suggested that the possibility that $Pu(OH)_4(am)$ changes into $PuF_3(s)$ as the solid phase limiting plutonium is low in this possible range of fluoride concentration.

5. 3. 4   Effect of SO_4^{2-} concentration (case I)

Plutonium sulphate complexes, of which the formation is considered in a reducing groundwater, are $Pu(SO_4)_n^{3-2n}$ (n=1, 2) of plutonium(III) and $Pu(SO_4)_n^{4-2n}$ (n=1, 2) of plutonium (IV). The influence of sulphur concentration on the plutonium solubility is investigated by the calculation for the saline water (case I). The complexation of sulphur concentration depends on the Eh-pH condition. The Eh and pH values in case I are assumed to vary from -200 to -50mV and from 6.0 to 8.0, respectively. Figure 5.13 shows the calculations for the various Eh-pH conditions at the sulphur concentration of 3×10^{-2} mol/l. Plutonium(III) sulphate complexes, Pu $(SO_4)_n^{3-2n}$(n=1, 2), are dominantly created in this Eh-pH range, while the remarkable formation of plutonium(IV) sulphate complexes, $Pu(SO_4)_n^{4-2n}$(n=1, 2), is not recognized in these analyses. In the Eh range of -150 to -50mV, the fraction of $Pu(SO_4)_n^{3-2n}$(n=1, 2) rises with decreasing pH value and accounts for over 90% at pH6.1 and pH6.5. The formation of $Pu(SO_4)_n^{3-2n}$(n=1, 2) is especially conspicuous in the pH range of weak acidity to neutrality. However, the fraction of

solid phase: $Pu(OH)_4(am)$, total sulphur concentration : 3×10^{-2} (mol/l)
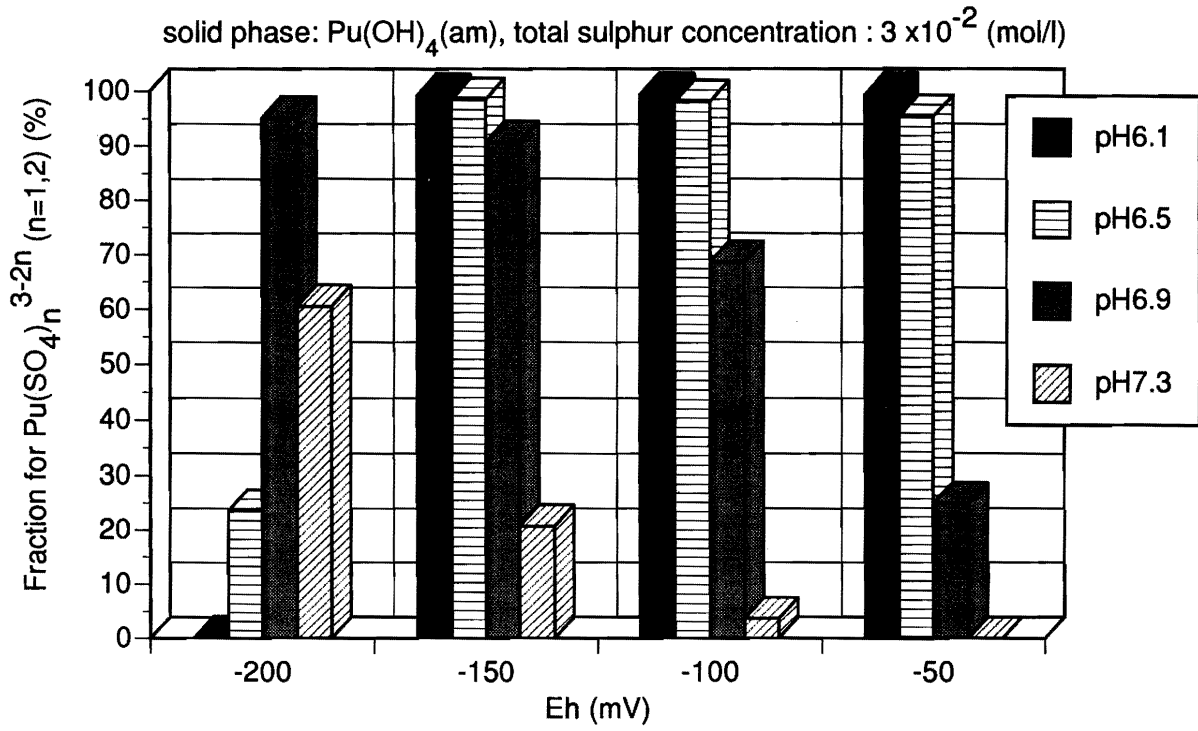

Fig. 5.13   Fraction of Pu(III) sulphur complexes at several Eh-pH conditions
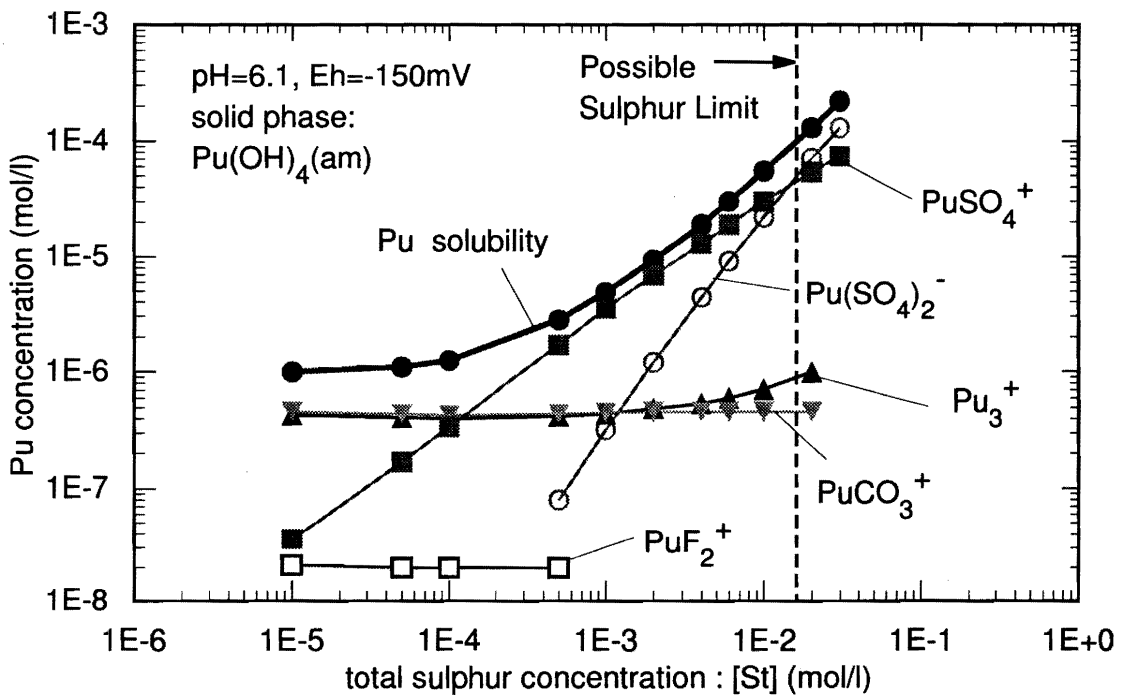
Fig. 5.14   Effect of sulphur concentration on plutonium solubility and speciation

sulphur complexes decreases below pH6.5 at -200mV because of the stability of SO_4^{2-} under such strong reducing condition.

The solubility and speciation at Eh-150mV and pH6.1, indicating the most conspicuous influence of SO_4^{2-}, are given in Fig. 5.14. The dominant aqueous species changes into $PuSO_4^+$ at the sulphur concentration of $> 5.0 \times 10^{-4}$ mol/l. The concentration of $Pu(SO_4)_2^-$ dominantly increases at the higher sulphur concentration. The change of the plutonium solubility is controlled by increasing concentration of $Pu(SO_4)_n^{3-2n}$(n=1, 2) at the sulphur concentration of $> 5.0 \times 10^{-4}$ mol/l.

The sulphur concentration estimated from the investigated chemical composition data varies from 5.2×10^{-7} to 1.6×10^{-2} mol/l as shown in Table 2.6. If the results in case I are estimated based on this range of sulphur concentration, it is suggested that $Pu(SO_4)_n^{3-2n}$(n=1, 2) of maximum 98% are dominantly formed in the reducing groundwater at low pH. The maximum solubility in the possible range of sulphur concentration is calculated to be about 1.3×10^{-4} mol/l. This solubility is two orders of magnitude higher than that with no influence of SO_4^{2-} ligand. High sulphur concentration causes a significant change of plutonium solubility and speciation from acid to neutral pH.

5. 3. 5 Effect of NO_3^- and NH_4^+ concentration (case J)

Nitrogen concentration may be enhanced in groundwater owing to leaching $NaNO_3$(s) from bituminized waste matrix. The effect of nitrogen concentration on plutonium solubility is

Fig. 5.15 Fraction of Pu(IV) nitrate complexes at Eh-200mV and total nitrogen concentration of 1×10^{-2} mol/l

estimated from the calculation for groundwater case J under various conditions of Eh-pH and carbon concentration, using the thermodynamic data of plutonium nitrate and ammoniate complexes in oxidation state of III to VI. The vari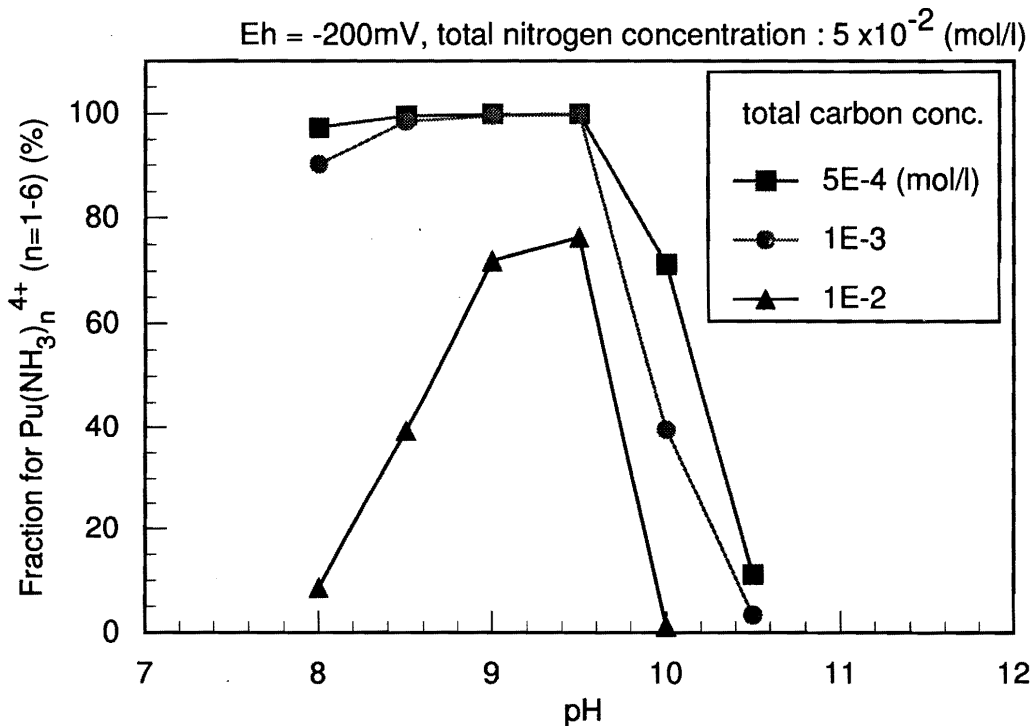ous carbon concentration is also assumed in calculation to research the competition on the complexation with carbon and nitrogen. Figure 5.15 shows the evaluation at Eh-200mV and total nitrogen concentration of 5×10^{-2} mol/l in alkaline pH. Plutonium (IV) ammoniate complexes are formed in reducing condition at high formation ratio in the pH range of 8 to 9.5. The fraction of the ammoniate complexes falls down over pH10. High carbon concentration in groundwater causes the decreasing formation of ammoniate complexes. The calculation at various Eh value from -400 to -100mV indicates the same results. Figure 5.16 shows the change of plutonium solubility as a function of total nitrogen concentration at pH9.5, Eh-200mV and total carbon concentration of 5×10^{-4} mol/l. High nitrogen concentration over 1×10^{-2} mol/l causes the increase of plutonium solubility. Dominant aqueous species changes into $Pu(NH_3)_6^{4+}$. Based on the discussion on the possible range of nitrogen concentration in section 2.3, the maximum nitrogen concentration in engineered barrier is assumed to be 2×10^{-2} mol/l. Taking account of the maximum level of nitrogen concentration, plutonium solubility may be about one order of magnitude higher owing to the formation of plutonium(IV) nitrate complexes. Figure 5.17 shows the dependance of plutonium solubilities on both nitrogen and carbon concentration. The effect of nitrogen concentration on plutonium solubility is restricted at low carbon concentration of $< 1 \times 10^{-3}$ mol/l and at high nitrogen concentration of $> 1 \times 10^{-2}$ mol/l. From the results for both case F and case I, plutonium solubility is more sensitive to the change of total carbon concentration than that of nitrogen concentration. It is suggested that
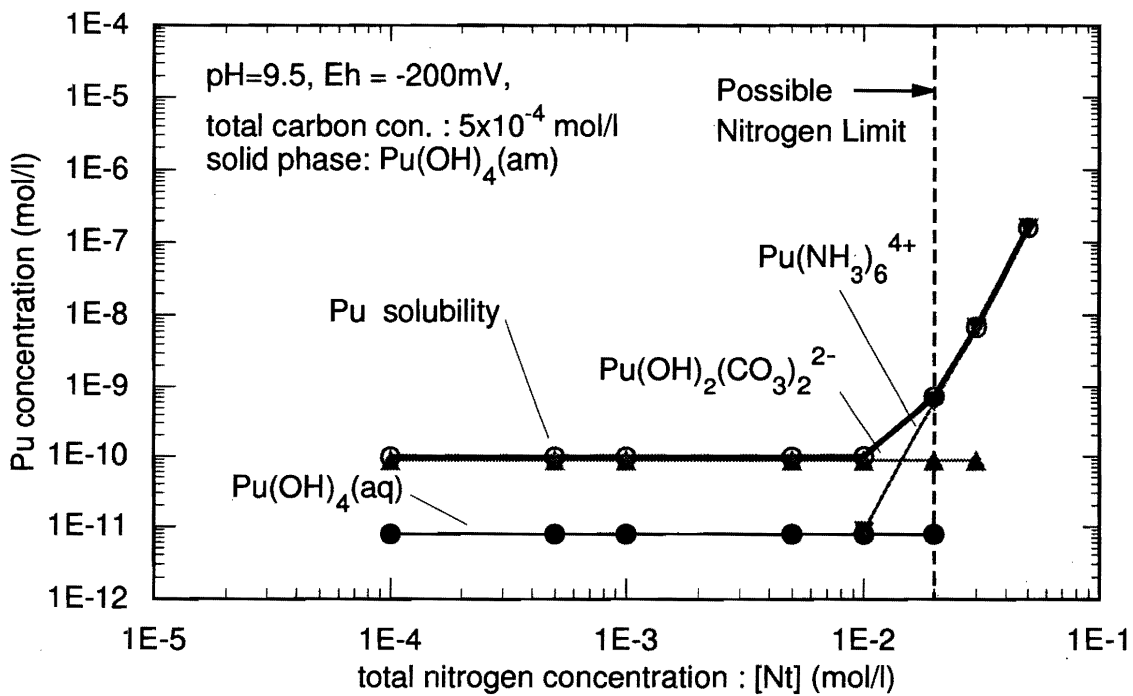
Fig. 5.16   Effect of nitrogen concentration on plutonium solubility and speciation
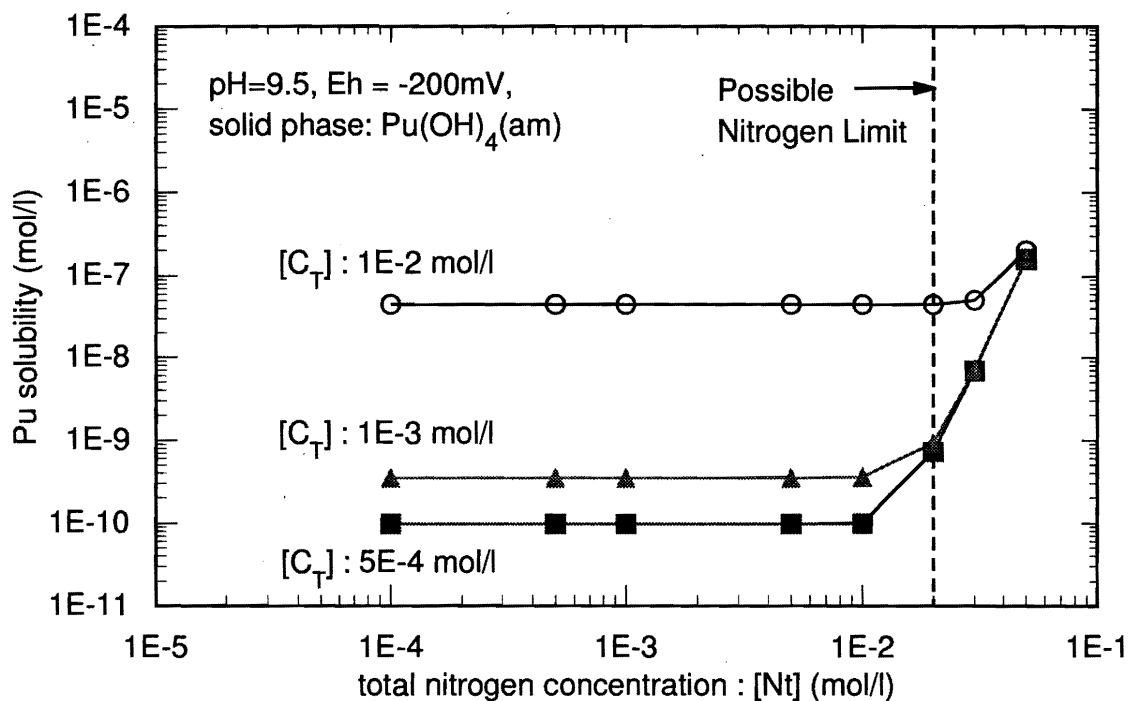
Fig. 5.17 Dependence of Pu solubilities on both nitrogen and carbon concentration at alkaline pH (total carbon concentration : [CT] = 5E-4, 1E-3 and 1E-2 mol/l)

nitrogen concentration hardly has an effect on plutonium solubility at alkaline pH.

5. 4 Plutonium solubility and speciation of case A to case J

The results of the solubility and speciation analyses of case A to case J for plutonium are summarized as follows.

● case A, caseB, case C (typical groundwater) :   From the results in case A to C, the reasonable solid phase limiting plutonium solubility can be basically regarded as $Pu(OH)_4(am)$. The dominant aqueous species in case A are plutonium(III) cationic forms, $PuCO_3^+$ and $PuSO_4^+$. Under the pH condition of neutrality to alkalinity, plutonium(III) cationic forms change into plutonium(IV) hydroxide-carbonate complexes, $Pu(OH)_2(CO_3)_2^{2-}$.

● case D (pH condition) :   The dominant species are estimated to be cationic forms of plutonium(III) under the pH condition of 6.0 to 7.0. In the pH range of 7.0 to 13.0, they change into plutonium(IV) hydroxide-carbonate complex, $Pu(OH)_2(CO_3)_2^{2-}$ or $Pu(OH)_4(CO_3)_2^{4-}$. The maximum plutonium solubility at acid pH is approximately 8.0×10^{-6} mol/l.

● case E (Eh condition) :   At pH6.0, the decrease of plutonium solubility is caused by the

change of the dominant aqueous species of plutonium(III) to (IV) with increasing Eh. At pH9.0, plutonium solubility is basically constant at higher Eh condition than about -400mV. The plutonium solubility within the Eh-pH condition under which plutonium(III) aqueous species is dominant depends on Eh parameter. In the case that plutonium(IV) aqueous species predominantly formed, plutonium solubility is hardly effected by Eh condition besides low Eh condition under which the formation of plutonium(IV) hydroxide-carbonate complexes is inhibited.

● case F (carbon concentration) : Plutonium solubility increases up to about 6.5×10^{-5} mol/l, taking account of the possible range of carbon concentration from 1×10^{-4} to 5×10^{-2} mol/l. The solubility at weak alkaline pH ($8 < pH < 9$) is about two orders of magnitude higher than that at strong pH ($> pH11$) at total carbon concentration of 5×10^{-2} mol/l. Dominant plutonium species in alkaline groundwater are estimated to be $Pu(OH)_n(CO_3)_2^{n-}$ (n=2,4) from the comparison between calculated and measured solubilities.

● case G (phosphorus concentration) : In the possible range of phosphorus concentration estimated from measurements, phosphorus ligand hardly have an effect on the plutonium solubility.

● case H (fluoride concentration) : Taking into account the maximum level of fluoride concentration, PuF^{2+} accounts for over 30% of aqueous plutonium species at the low pH. The solubility slightly changes from 1.6×10^{-6} to 2.4×10^{-6} mol/l with increasing fluoride concentration. It is suggested that the possibility that $Pu(OH)_4$(am) changes into PuF_3(s) as the solid phase limiting plutonium is low in this possible range of fluoride concentration.

● case I (sulphur concentration) : The maximum ratio of $Pu(SO_4)_n^{3-2n}$ (n=1, 2) amounts to about 98% under the influence of SO_4^{2-} ligand. The plutonium solubility is suggested to increase up to about 1.3×10^{-4} mol/l on account of the formation of $Pu(SO_4)_n^{3-2n}$ (n=1, 2). High sulphur concentration causes a significant change of plutonium solubility and speciation from acid to neutral pH.

● case J (nitrogen concentration) : The effect of nitrogen concentration on plutonium solubility is restricted at low carbon concentration of $< 1 \times 10^{-3}$ mol/l, at high nitrogen concentration of $> 1 \times 10^{-2}$ mol/l. Under the nitrogen concentration limit of 2×10^{-2} mol/l, plutonium solubility is more sensitive to the change of total carbon concentration than that of nitrogen concentration. It is suggested that nitrogen concentration hardly has an effect on plutonium solubility at alkaline pH.

6. Technetium Results

6.1 Saline water (case A), fresh water (case B) and simulated bentonite water (case C)

Solid phase limiting technetium solubility is examined through the solubility and speciation analysis for three kinds of the typical groundwater, saline water (case A), fresh water (case B) and simulated bentonite water (case C). In reducing environment, the solid phase limiting technetium solubility is considered to be $TcO_2(c)$ or $TcO_2 \cdot 2H_2O$. Table 6.1 shows the solubility and speciation in case A, B and C. The solubilities of $TcO_2(c)$ and $TcO_2 \cdot 2H_2O$ are in same order for these chemical compositions of case A to C. The various chemical composition in three kinds of groundwater hardly have a influence on technetium solubility. The solubility of $TcO_2 \cdot 2H_2O$ is calculated to vary from 5.7×10^{-9} to 6.4×10^{-9} mol/l. The solubilities of $TcO_2 \cdot nH_2O$ have been measured by Meyer, R. E.(1991)[51] and Eriksen, T. E.(1993)[43]. The measured solubility of $TcO_2 \cdot nH_2O$ by Eriksen, T. E.(1993) indicates the level of 10^{-9} to 10^{-8} mol/l at constant CO_2 partial pressure at neutral pH. The solubility of $TcO_2 \cdot 1.63H_2O$ by Meyer, R. E. (1991) ranges from 10^{-9} to 10^{-8} mol/l. Although the chemical composition in their experiments are different from that used in these calculations, the analyzed solubilities of $TcO_2 \cdot 2H_2O$ are consistent with these experimental data. The calculated solubility of $TcO_2(c)$ is approximately 4 orders of magnitude lower than that of $TcO_2 \cdot 2H_2O$. Technetium hydrous oxide, $TcO_2 \cdot 2H_2O$, is considered to be more suitable for the solid phase restricting the technetium solubility

Table 6.1   The solubilities and speciation of Tc for saline water (caseA), fresh water (case B) and simulated bentonite water (case C).

Type of water	pH Eh (mV)	solubility (mol/l)		speciation (%)
		$TcO_2(c)$	$TcO_2 \cdot 2H_2O$	
Saline water (case A)	6.9 -200	3.2×10^{-13}	6.4×10^{-9}	TcO(OH)2(aq) 82.4 Tc(OH)2CO3(aq) 16.3 (TcO2(OH)2)2(aq) 1.3
Fresh water (case B)	7.4 -200	2.8×10^{-13}	6.0×10^{-9}	TcO(OH)2(aq) 92.6 Tc(OH)2CO3(aq) 5.9 (TcO2(OH)2)2(aq) 1.5
Simulated bentonite water (case C)	9.0 -397	2.7×10^{-13}	5.7×10^{-9}	TcO(OH)2(aq) 96.0 TcO(OH)3⁻ 2.0 (TcO2(OH)2)2(aq) 1.5

than $TcO_2(c)$, taking into account the concervative solubility. The dominant aqueous species is suggested to be technetium(IV) hydroxide, $TcO(OH)_2(aq)$, which accounts for over 80% of all technetium aqueous species.

6. 2　Effect of pH and Eh conditions (case D and case E)

The effect of pH condition on technetium solubility is investigated from the analyses for the groundwater of case D shown in Table 2.5. The groundwater is assumed to be constant at Eh-200mV and varying from pH6.0 to 13.0. The solubility and speciation for case D are given in Fig. 6.1. The solid phase of technetium is assumed to be $TcO_2 \cdot 2H_2O$. In the pH range of 6.0 to 9.6, the solubility is constant at about 6×10^{-9} mol/l, and the dominant aqueous species is estimated to be $TcO(OH)_2(aq)$. Over pH9.6, however, the solubility and aqueous speciation vary dramatically. The solubility increases up to 1.0×10^{-2} mol/l at pH11.5 owing to changing into TcO_4^- as dominant species.

Technetium solubility for the groundwater of case E is calculated assuming the constant pH and various Eh values. The solubility depending on Eh values is described at two kinds of constant pH condition, pH6.0 and pH9.0. Figure 6.2 shows the solubility and aqueous speciation at pH6.0. The Eh value at pH6.0 ranges from -200 to +200mV. The solubility of $TcO_2 \cdot 2H_2O$ sharply increases over about +100mV because of the change of oxidation state from technetium (IV) to (VII). In the Eh range of -200 to +100mV, $TcO(OH)_2(aq)$ is predominant in technetium
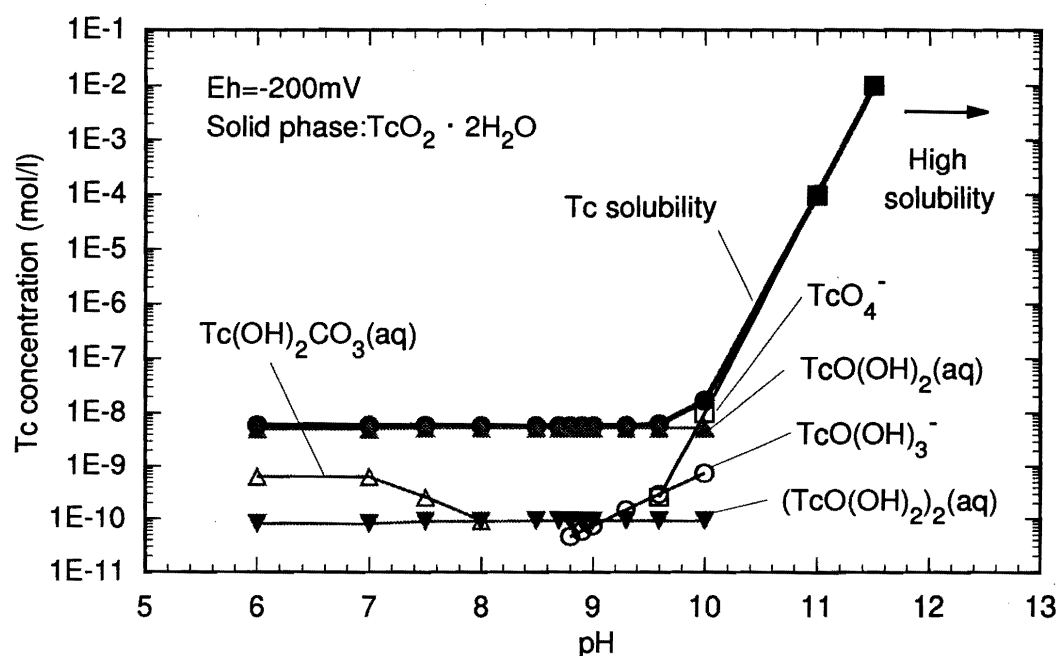
Fig. 6.1　Technetium solubility and speciation for the groundwater (case D) assuming the constant Eh (-200mV) and the pH range of 6.0 to 13.0.
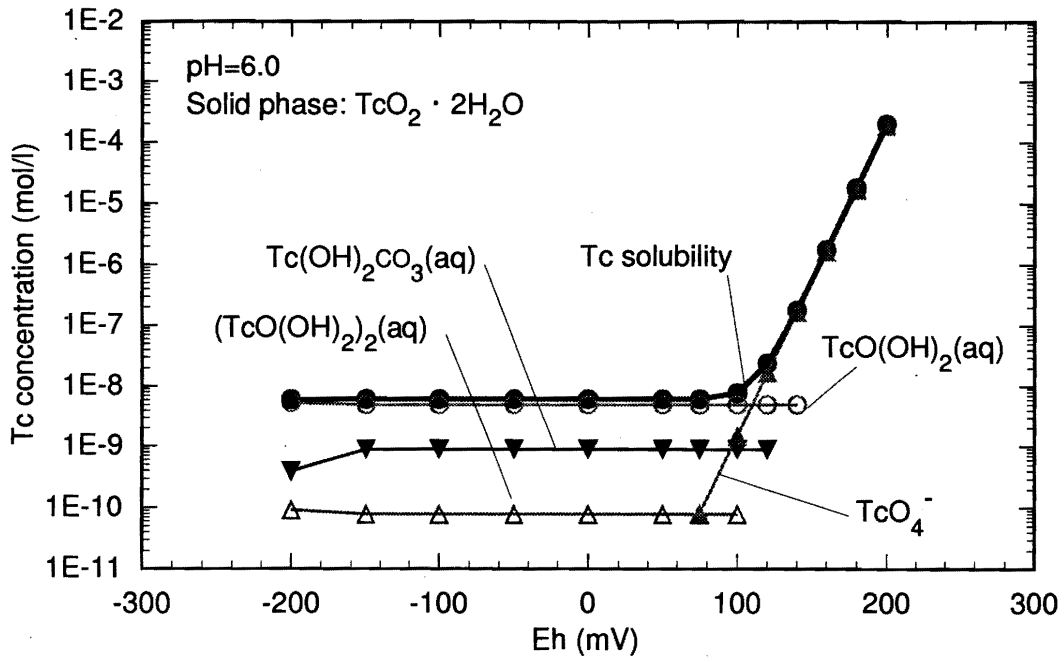
Fig. 6.2 Technetium solubility and speciation for the groundwater (case E) assuming the constant pH6.0 and the Eh range of -200 to +200mV.
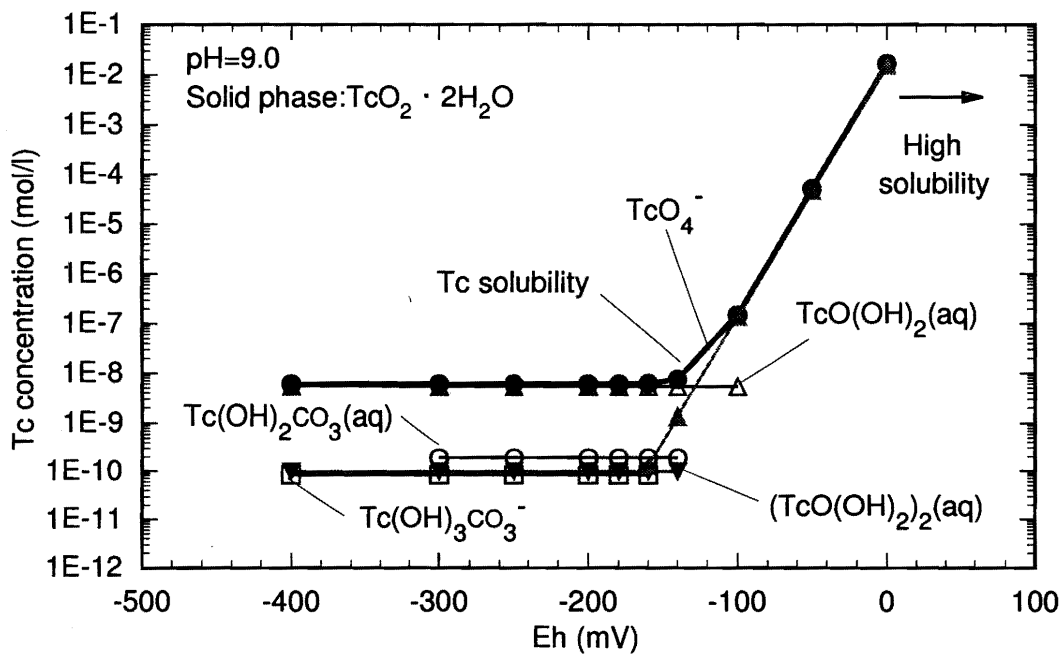
Fig. 6.3 Technetium solubility and speciation for the groundwater (case E) assuming the constant pH9.0 and the Eh range of -400 to +100mV.
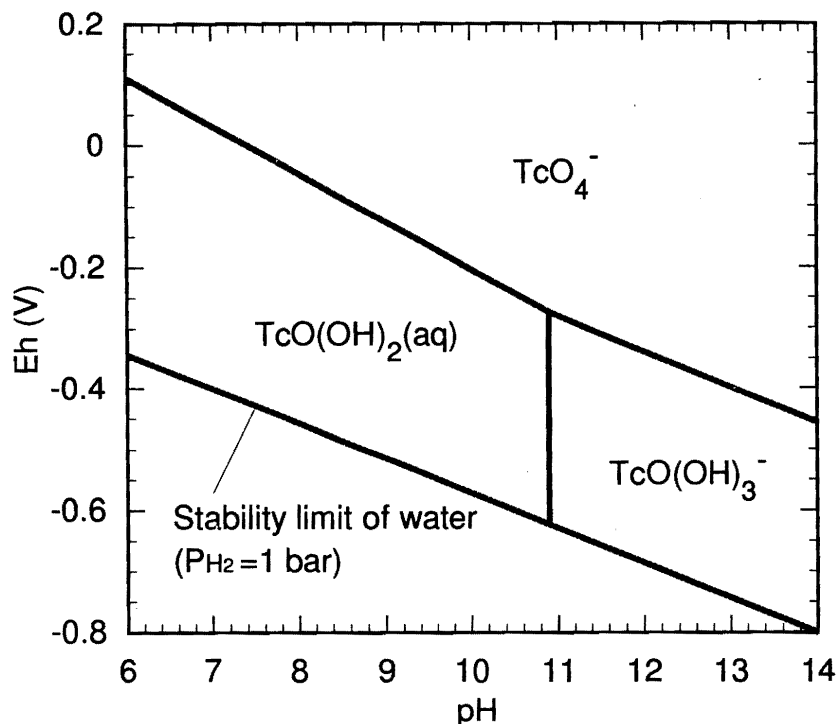
Fig. 6.4 Technetium aqueous phase in Tc-O-H system

aqueous species, and the solubility is calculated to be constant. Over Eh+100mV, the change of the technetium solubility is controlled by the increasing formation ratio of TcO_4^-. The solubility of $TcO_2 \cdot 2H_2O$ is calculated to increase up to 2.0×10^{-4} mol/l at pH6.0 and Eh+200mV.

Figure 6.3 shows the solubility profile calculated in case E at pH9.0. The Eh condition at pH9.0 varies from -400 to +100mV. The solubility profile for $TcO_2 \cdot 2H_2O$ at pH9.0 indicates the same trend for various Eh condition at pH6.0. The solubility of $TcO_2 \cdot 2H_2O$ sharply increases at about -120mV owing to the enhanced formation of TcO_4^-. The high solubility of $> 1 \times 10^{-1}$ mol/l is calculated over Eh $\pm$ 0mV.

From the results of case D and case E, the Eh-pH condition, under which TcO_4^- is dominantly formed, leads to the increase of the technetium solubility. It is suggested that the Eh-pH condition has a great influence on the technetium solubility. Figure 6.4 shows the boundary between technetium (IV) and (VII) in Eh-pH diagram of technetium. From the calculations in case E, it is inferred that the technetium solubility is enhanced in the Eh-pH region where technetium (VII) (TcO_4^-) is stable.

6. 3   Effect of various ligand concentration

6. 3. 1   Effect of CO_3^{2-} concentration (case F)

The complexation of ligand, CO_3^{2-} with technetium (IV) has been described in the solubility

experiment of Eriksen, T. E. et al. (1993)[43]. Eriksen, T. E. et al. (1993) indicated three kinds of technetium(IV) hydroxide-carbonate complexes from their solubility experiment under constant $CO_2(g)$ partial pressure. The equilibrium constants of $Tc(OH)_2CO_3(aq)$ and $TcOH(CO_3)_2^-$ in their experiment are selected in this data base. Yamaguchi, T. and Takeda, S. (1999)[9], however, pointed out that the equilibrium constant of $Tc(OH)_3CO_3^-$ was overestimated, judging from pH dependance of solubility experiment in Eriksen, T. E. et al. (1993). Yamaguchi, T. and Takeda, S. (1999) modified the equilibrium constant of $Tc(OH)_3CO_3^-$ based on the equilibrium constant for the hydrolysis of $TcO(OH)_2(aq)$. The effect of carbonate concentration is estimated from the analysis for the groundwater of case F, taking account of various carbon concentration. The pH dependance on technetium solubility and speciation at the constant carbon concentration of 5×10^{-2} mol/l and Eh -300mV is shown in Fig. 6.5. The formation of $Tc(OH)_2CO_3(aq)$ indicates high ratio at pH8.0 and decreases with increasing pH. Over pH10.0, the fraction of $TcO(OH)_3^-$ exceeds that of $Tc(OH)_2CO_3(aq)$. The other technetium(IV) hydroxide-carbonate complexes, $Tc(OH)_3CO_3^-$ and $TcOH(CO_3)_2^-$, are hardly created in this chemical composition. With respect to Eh dependance, this formation ratio does not change within the Eh conditions under which technetium(IV) aqueous species become stable. Figure 6.6 shows the solubility and speciation analyzed at pH8.0 and Eh-300mV, indicating the most conspicuous effect of carbon concentration. The solubility of $TcO_2 \cdot 2H_2O$ is nearly constant as shown in Fig. 6.5. The maximum formation ratio of $Tc(OH)_2CO_3(aq)$ accounts for only 27% at the carbonate concentration of 5×10^{-2} mol/l
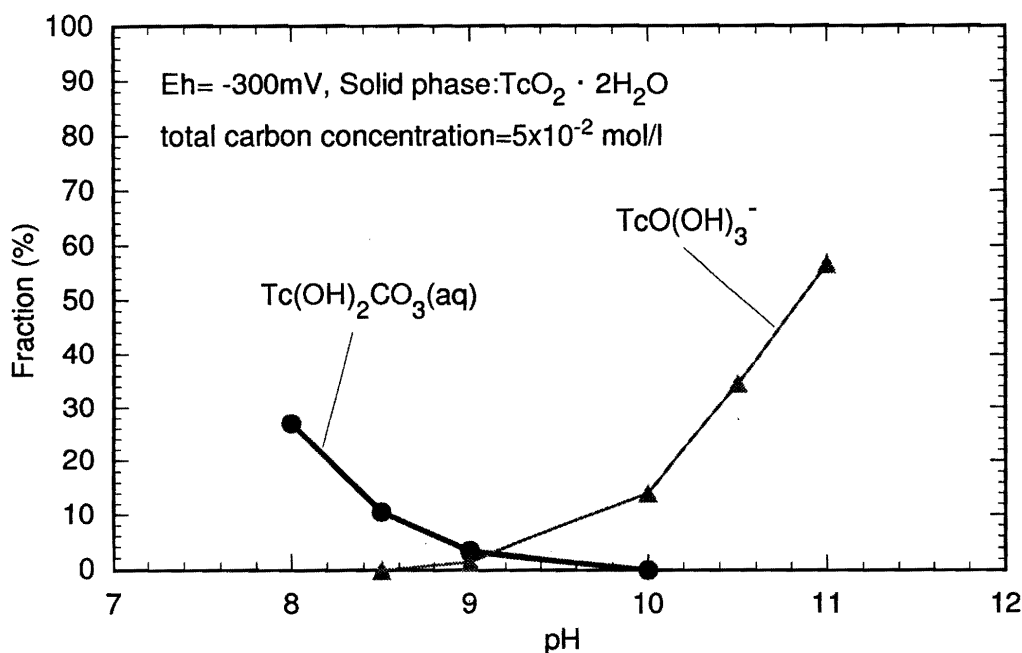
Fig. 6.5   Formation ratio as a function of pH at Eh-300mV and high carbon concentration of 5×10^{-2} mol/l
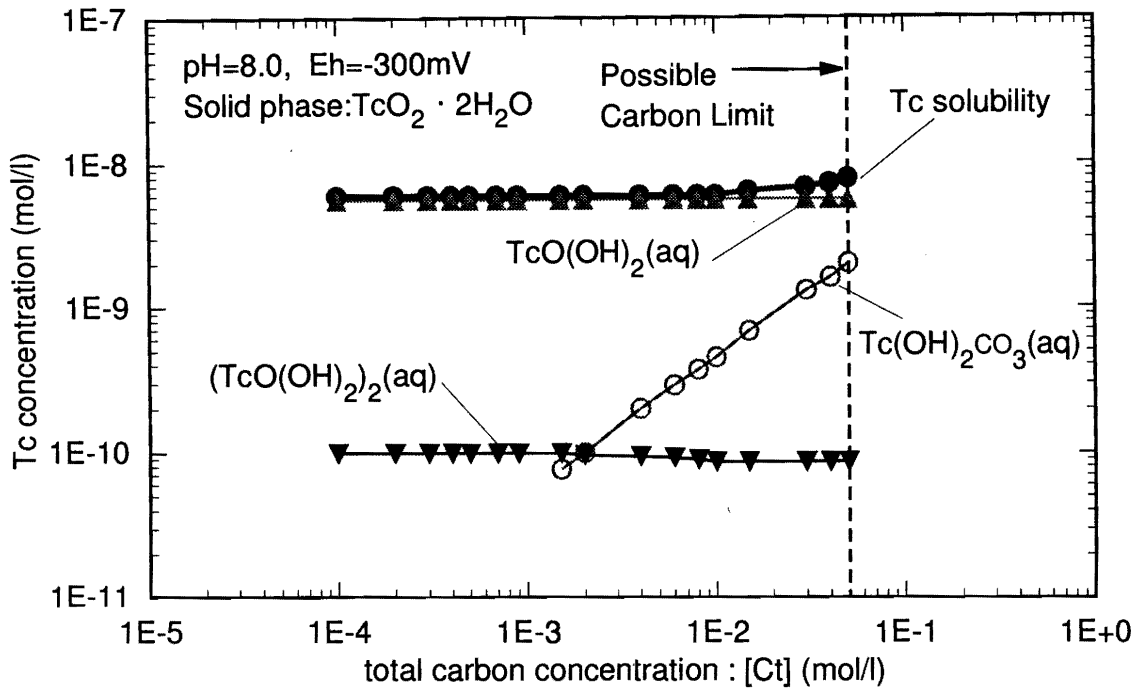
Fig. 6.6 Technetium solubility and speciation for the groundwater (case F) assuming the range of carbon concentration of 1×10^{-4} to 5×10^{-2} mol/l

according to increasing carbon concentration, but the dominant species remains $TcO(OH)_2(aq)$ in spite of carbon concentration level.

The possible carbon concentration determined from the investigated chemical composition data ranges from 1.6×10^{-4} to 5×10^{-2} mol/l as shown in Table 2.6. $Tc(OH)_2CO_3(aq)$ of 27% is created in a reducing environment, based on this range of the possible carbonate concentration. However, the increasing concentration of $Tc(OH)_2CO_3(aq)$ scarcely contribute to the change of the technetium solubility. There is no formation of $Tc(OH)_2CO_3(aq)$ under high pH condition of > pH10.0. The speciation under the high pH condition is controlled by technetium hydroxides, $TcO(OH)_2(aq)$ and $TcO(OH)_3^-$. It is suggested that the concentration of CO_3^{2-} ligand does not especially influence on the technetium solubility at alkaline pH.

6. 3. 2 Effect of SO_4^{2-} concentration (case I)

Formation of technetium(IV) sulphate complexes, $TcO(SO_4)_n^{2-2n}$ (n=1 to 5), is inferred under a reducing condition. The effect of sulphur concentration on the technetium solubility is estimated from the calculation for the saline water of case I. Several Eh-pH conditions used here are assumed to be in the Eh range of -200 to +50mV and the pH range of 6.0 to 8.0. From the calculation assuming high sulphur concentration of 3×10^{-2} mol/l, the dominant aqueous species is estimated to be $TcO(OH)_2(aq)$ or TcO_4^- within this Eh-pH range. The formation of sulphate complexes, $TcO(SO_4)_n^{2-2n}$ (n=1 to 5), is not predominantly recognized in this chemical composition

of case I. The maximum concentration of SO_4^{2-} estimated from the investigated composition data is 1.6×10^{-2} mol/l as shown in Table 2.6. Based on the possible range of sulphur concentration, it is inferred that the technetium solubility and speciation are hardly influenced by sulphur concentration in a natural groundwater.

6. 3. 3　Effect of NO_3^- and NH_4^+ concentration (case J)

In an engineered barrier system, nitrogen concentration may be enhanced owing to leaching from the waste matrix including a large quantity of $NaNO_3(s)$. The thermodynamic data for nitrate and ammoniate complexes, $TcO(NO_3)_n^{2-n}$ (n=1 to 5) and $TcO(NH_3)_n^{2+}$ (n=1 to 5) are considered in this data base to estimate the effect of nitrogen concentration. The effect of nitrogen concentration on technetium solubility is examined in calculation for groundwater of case J. Figure 6.7 indicates formation ratio of technetium aqueous species at alkaline pH, Eh-300mV, carbon concentration of 5×10^{-2} mol/l and nitrogen concentration of 5×10^{-2} mol/l . Technetium (IV) ammoniate complex, $TcO(NH_3)_5^{2+}$, is dominantly formed in the pH range of 8 to 12. The formation of $TcO(NH_3)_5^{2+}$ also appears under other pH-Eh condition for case J listed in Table 2.5. Figure 6.8 shows the solubility change as a function of nitrogen concentration at pH9.5 and Eh-300mV. At nitrogen concentration of > about 1×10^{-3} mol/l, technetium solubility increases owing to the formation of $TcO(NH_3)_5^{2+}$. Technetium solubility is evaluated to be over 1×10^{-3} mol/l at the nitrogen concentration of 2×10^{-2} mol/l. The maximum nitrogen concentration
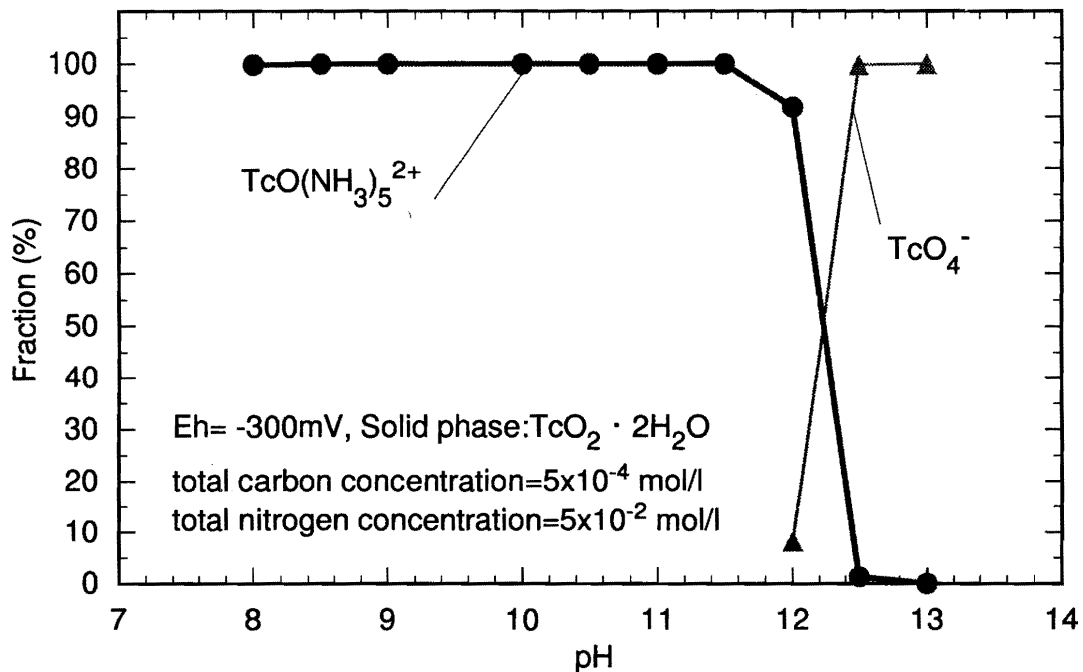
Fig. 6.7　Formation ratio as a function of pH at Eh-300mV, carbon concentration of 5×10^{-2} mol/l and nitrogen concentration of 1×10^{-1} mol/l
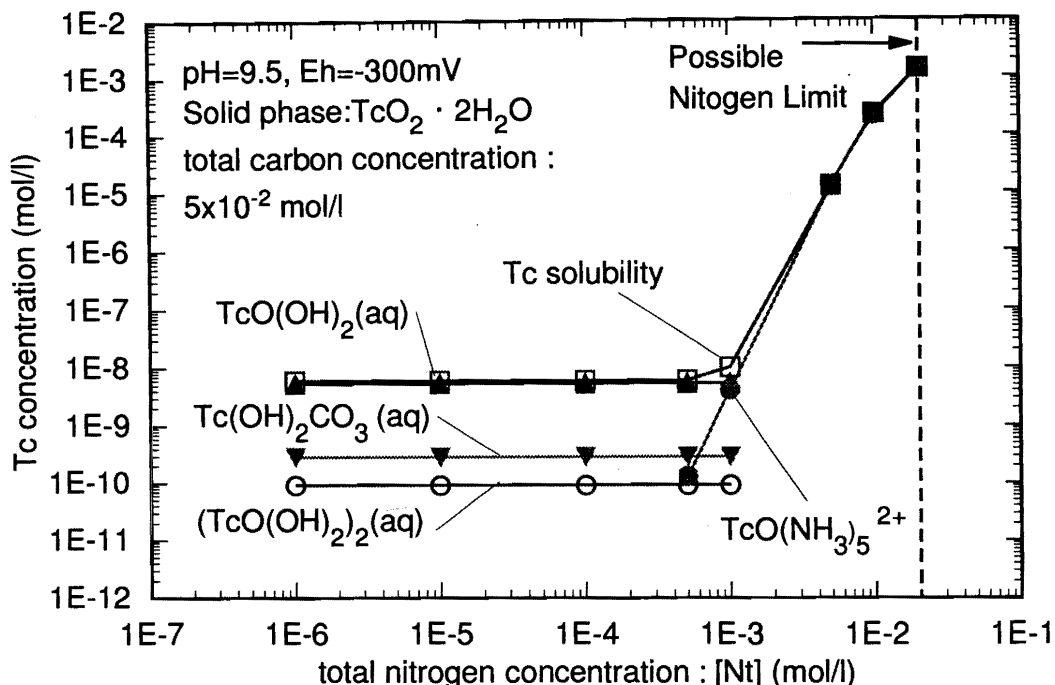
Fig. 6.8 Effect of nitrogen concentration on technetium solubility and speciation

including in groundwater is assumed to be 2×10^{-2} mol/l as discussed in section 2.3. Taking account of such concentration level, high nitrogen concentration of $> 1 \times 10^{-3}$ mol/l may enhance technetium solubility in reducing environment. This calculation indicates that technetium solubility at alkaline pH and reducing Eh is enhanced owing to high nitrogen concentration. The thermodynamic data for $TcO(NO_3)_n^{2-n}$ (n=1 to 5) and $TcO(NH_3)_n^{2+}$ (n=1 to 5) have been estimated from model prediction by Brown, P. L. and Wanner, H. (1987)[33]. In order to estimate the effect of nitrogen concentration on technetium solubility more accurately, it is necessary to provide the more reliable data with a basis of experimental studies.

6. 4 Technetium solubility and speciation of case A to case J

The results analyzed for all the case of technetium are summarized as follows.

● case A, case B, case C (typical groundwater) : There is no difference of the solubilities and speciation of technetium for three kinds of the typical groundwater. $TcO_2 \cdot 2H_2O$ is more suitable for the solid phase restricting the technetium solubility than $TcO_2(c)$. Solubility of $TcO_2 \cdot 2H_2O$ is evaluated to be about 6×10^{-9} mol/l. The dominant aqueous species is suggested to be technetium(IV) hydroxide, $TcO(OH)_2(aq)$, which accounts for over 80% of all technetium aquious species.

● case D (pH condition) : Technetium solubility varies from 6×10^{-9} to 1×10^{-2} mol/l because

dominant aqueous species changes from $TcO(OH)_2(aq)$ to TcO_4^-.

● case E (Eh condition) :   The solubility of $TcO_2 \cdot 2H_2O$ sharply increases owing to the change of oxidation state from technetium (IV) to (VII). The Eh-pH condition, under which TcO_4^- is dominantly formed, leads to the increase of the technetium solubility. It is suggested that the Eh-pH condition has a great influence on the technetium solubility.

● case F (carbonate concentration) : $Tc(OH)_2CO_3(aq)$ of 27% is formed in a reducing environment at total carbon concentration of 5×10^{-2} mol/l. However, the increasing concentration of $Tc(OH)_2CO_3(aq)$ scarcely contribute to the change of the technetium solubility. There is no formation of $Tc(OH)_2CO_3(aq)$ under high pH condition of > pH10.0. The speciation for technetium is controlled by technetium hydroxides, $TcO(OH)_2(aq)$ and $TcO(OH)_3^-$. It is suggested that the concentration of CO_3^{2-} ligand does not especially influence on the technetium solubility at alkaline pH.

● case G and H (phosphorus and fluoride concentration) :   There is no existence of technetium phosphorus and fluoride complexes which has been proved by experimental study.

● case I (sulphur concentration) :   The formation of $TcO(SO_4)_n^{2-2n}$ (n=1 to 5) is not predominantly recognized in the Eh range of -200 to +50mV and the pH range of 6.0 to 8.0. It is inferred that the technetium solubility and speciation are hardly influenced by sulphur concentration in a natural groundwater.

● case J (nitrogen concentration) :   At nitrogen concentration of > about 1×10^{-3} mol/l, technetium solubility increases owing to the formation of $TcO(NH_3)_5^{2+}$. Technetium solubility is evaluated to be over 1×10^{-3} mol/l at nitrogen concentration of 2×10^{-2} mol/l and strongly depends on nitrogen concentration at alkaline pH and reducing Eh.

7. Conclusion

Solubility and speciation of americium, plutonium and technetium were calculated for 10 different chemical properties characterized by various pH-Eh condition and ligand concentration. In this study, the effect of these chemical properties on the solubility and speciation is discussed with for two pH regions. This is based on the following:

— Solubility and speciation of elements basically depends on pH condition.
— Natural groundwater in reducing environment indicates neutral or weak-alkaline pH, while interstitial water in bentonite or cement materials indicates higher alkaline pH .

Taking account of the discussion in section 2, the pH range applied in the calculations is divided into pH region I (6<pH<8) for natural groundwater and pH region II (8<pH<13) for interstitial water in buffer materials. The realistic solubility of each element is evaluated based on the result for the simulated bentonite water (case C).

7. 1 Americium solubility and speciation in a reducing groundwater

Solid phase and realistic solubility Table 7.1 shows the summary of americium solubility and speciation analyses in a reducing groundwater. Taking into account the condition of CO_2 partial pressure in groundwater, the solid phase limiting the americium solubility is adequate to be $AmOHCO_3(c)$. However, $Am(OH)_3(c)$ is considered to be more stable than $AmOHCO_3(c)$ under the condition of low carbonate concentration, strong alkaline pH or low Eh condition at which carbonate or bicarbonate ion is unstable. The realistic solubility of $AmOHCO_3(c)$ in reducing environment is estimated to be 5.0×10^{-7} mol/l from calculation in case C.

pH region I (6<pH<8) Dominant aqueous species are estimated to be cationic forms of americium(III) such as $AmCO_3^+$, $AmOH^{2+}$ and Am^{3+} in pH region I (6<pH<8). Under the effect of fluoride and sulphur concentration, the maximum ratio of formation for AmF_2^+ and $Am(SO_4)_n^{3-2n}$(n=1, 2) accounts for about 30% at pH6.2 and 90% at pH6.1, respectively. The chemical factors which have an effect on americium solubility within this pH region are considered to be pH condition, carbon and sulphur concentrations. Americium solubility increases with decreasing pH value. In particular, Americium solubility is calculated to increase up to about 2.0×10^{-4} mol/l owing to the formation of $Am(SO_4)_n^{3-2n}$(n=1, 2) from case I. Phosphorus and fluoride concentrations in groundwater hardly have an effect on americium solubility.

pH region II (8<pH<13) Americium solubility and speciation in pH region II (8<pH<13) especially depends on pH condition and carbon concentration. In accordance with

Table 7.1   Americium solubility and speciation in pH region I (6<pH<8) and pH region II (8<pH<13)

speciation	Region I (6<pH<8)	: $AmCO_3^+$, $AmOH^{2+}$, Am^{3+}, AmF^{2+} (max. 30%, pH6.2), $Am(SO_4)_n^{3-2n}$(n=1,2) (max. 90%, pH6.1)
	Region II (8<pH<13)	: $Am(OH)_2CO_3^{2+}$ → $AmOH(CO_3)_2^{2-}$ → $Am(CO_3)_3^{3-}$ (according to increasing CO_3^{2-} concentration)
solubility (mol/l)	Solid phase : $AmOHCO_3(c)$ or $Am(OH)_3(c)$ (low Eh, strong alkaline pH or low CO_3^{2-} concentration) Realistic solubility : 5.0×10^{-7} (from case C)	
	Region I (6<pH<8)	: Max. 2.0×10^{-4} (Key parameter : pH, CO_3^{2-} and SO_4^{2-} concentration)
	Region II (8<pH<13)	: Max. 2.0×10^{-5} (Key parameter : pH and CO_3^{2-} concentration)

increasing carbon concentration, americium dominant species changes in this pH region as the following ; $Am(OH)_2CO_3^-$ → $AmOH(CO_3)_2^{2-}$ → $Am(CO_3)_3^{3-}$. At total carbon concentration of 5.0×10^{-2} mol/l, americium solubility increases up to about 2.0×10^{-5} mol/l at pH10 and falls down to 3×10^{-9} mol/l at pH13 as shown in Fig. 4.4. This decrease of solubility in strong alkaline pH is based on the change of solid phase from $AmOHCO_3(c)$ to $Am(OH)_3(c)$. The maximum solubility is 2.0×10^{-5} mol/l at pH10 and total carbon concentration of 5.0×10^{-2} mol/l. The effect of ammoniate concentration can be ignored based on the calculation in case J.

7. 2   Plutonium solubility and speciation in a reducing groundwater

Solid phase and realistic solubility   Table 7.2 shows the summary of plutonium solubility and speciation analyses in a reducing groundwater. Taking into account the conservative solubility value, the solid phase limiting plutonium solubility is adequate to be $Pu(OH)_4(am)$. The realistic solubility of $Pu(OH)_4(am)$ in reducing environment is estimated to be 4.0×10^{-7} mol/l from the calculation in case C.

pH region I (6<pH<8)   Dominant aqueous species are estimated to be cationic forms of plutonium(III) such as $PuCO_3^+$ and Pu^{3+} in pH region I (6<pH<8). Such plutonium(III) aqueous species changes into plutonium(IV) hydroxide-carbonate complex, $Pu(OH)_2(CO_3)_2^{2-}$ at about pH7.5. The maximum ratio of formation for $Pu(HPO_4)_4^{4-}$ and PuF^{2+} accounts for about 12% at pH6.2 and 30% at pH6.2, respectively, taking account of the possible range of phosphorus and

Table 7.2 Plutonium solubility and speciation in pH region I (6<pH<8) and pH region II (8<pH<13)

speciation	Region I (6<pH<8)	: $PuCO_3^+$, $Pu^{3+} \rightarrow Pu(OH)2(CO3)2^{2-}$ (over about pH7.5) $Pu(HPO4)4^{4-}$ (max. 12%, pH6.2), PuF^{2+} (max. 30%, pH6.2), $Pu(SO4)n^{3-2n}(n=1,2)$ (max. 98%, pH6.1)
	Region II (8<pH<13)	: $Pu(OH)2(CO3)2^{2-} \rightarrow Pu(OH)4(CO3)2^{4-}$ (according to increasing pH value)
solubility (mol/l)		Solid phase : Pu(OH)4(am)
		Realistic solubility : 4.0×10^{-7} (from case C)
	Region I (6<pH<8)	: Max. 1.3×10^{-4} (Key parameter : Eh, pH, $CO3^{2-}$ and $SO4^{2-}$ concentration)
	Region II (8<pH<13)	: Max. 6.5×10^{-6} (Key parameter : pH and $CO3^{2-}$ concentration)

fluoride concentration. Plutonium(III) sulphur complexes, $Pu(SO_4)_n{}^{3-2n}(n=1, 2)$, of maximum 98% may exist at pH6.1 and Eh-150mV. Key chemical parameters are estimated to be Eh-pH condition, $CO_3{}^{2-}$ and $SO_4{}^{2-}$ ligands. Plutonium solubility is enhanced by the Eh-pH condition under which plutonium(III) aqueous species is dominantly formed. In pH region I, plutonium solubility has a great effect on sulphur concentration and increases up to 1.3×10^{-4} mol/l at sulphur concentration of 1.6×10^{-2} mol/l.

pH region II (8<pH<13) Plutonium solubility and speciation in pH region II are controlled by chemical factors of pH and $CO_3{}^{2-}$ ligand. Dominant aqueous species of plutonium changes from $Pu(OH)_2(CO_3)_2{}^{2-}$ to $Pu(OH)_4(CO_3)_2{}^{4-}$ according to increasing pH value. The solubility of $Pu(OH)_4$(am) in weak alkaline pH range (8<pH<9) is about 2 orders of magnitude higher than that in strong alkaline pH range (> pH11) at total carbon concentration of 5×10^{-2} mol/l. The solubility increases up to about 6.5×10^{-5} mol/l, taking account of the possible range of carbon concentration from 1×10^{-4} to 5×10^{-2} mol/l. From the result in case J, nitrogen concentration hardly has an effect on plutonium solubility at alkaline pH.

7. 3　Technetium solubility and speciation in a reducing groundwater

Solid phase and realistic solubility Table 7.3 shows the summary of technetium solubility and speciation analyses in a reducing groundwater. Technetium hydrous oxide, $TcO_2 \cdot 2H_2O$, is

Table 7.3   Technetium solubility and speciation in pH region I (6<pH<8) and pH region II (8<pH<13)

speciation	Region I (6<pH<8)	: TcO(OH)2(aq) or TcO4⁻ (at pH6 over Eh+100mV)
	Region II (8<pH<13)	: TcO(OH)2(aq) → TcO(OH)3⁻ (with increasing pH value) or TcO4⁻ (at pH9 over Eh-140mV) Tc(OH)2CO3(aq) (max. 27%, pH9) TcO(NH3)5²⁺ (max. 100%, over NH4⁺ con. of 10⁻³ mol/l)
solubility (mol/l)		Solid phase : TcO2 · 2H2O Realistic solubility : 6x10⁻⁹ (from case C) Region I (6<pH<8) : Max. 2.0x10⁻⁴ (Key parameter : Eh-pH condition) Region II (8<pH<13) : Max. > 10⁻¹ (high solubility) (Key parameter : Eh-pH condition and NH4⁺ concentration)

considered to be more suitable for the solid phase restricting the technetium solubility than TcO_2 (c), taking into account the concervative solubility. The realistic solubility of $TcO_2 \cdot 2H_2O$ is estimated to be 6×10^{-9} mol/l from calculation in case C.

pH region I (6<pH<8)   Technetium dominant aqueous species is either $TcO(OH)_2$(aq) or TcO_4^- in the pH region I. The formation ratio of TcO_4^- increases over Eh+100mV at pH6.0. The change from technetium(IV) to (VII) depends on Eh-pH condition and enhances the solubility of $TcO_2 \cdot 2H_2O$. From the calculation in case F, the solubility is evaluated to increase up to 2.0×10^{-4} mol/l owing the formation of TcO_4^-.

pH region II (8<pH<13)   In pH region II (8<pH<13), dominant aqueous species varies from $TcO(OH)_2$(aq) to $TcO(OH)_3^-$, according to increasing pH value. At pH 9 over Eh-140mV, the dominant species also changes from $TcO(OH)_2$(aq) to TcO_4^-. Technetium(IV) hydroxide-carbonate complex, $Tc(OH)_2CO_3$(aq), is estimated to exist at maximum ratio of 27%. This suggests that carbon concentration in groundwater has little influence on technetium solubility under alkaline pH conditions. The formation of $TcO(NH_3)_5^{2+}$ is recognized over high ammoniate concentration of 1.0×10^{-3} mol/l. Chemical factors of Eh-pH condition and ammoniate concentration have a significant effect on technetium solubility and speciation. Maximum solubility of $TcO_2 \cdot 2H_2O$ is calculated to be over 1×10^{-1} mol/l in pH region II.

Acknowledgment

REFERENCES

(1) Parkhurst, D. L., et al. : PHREEQE-A Computer Program for Geochemical Calculations, U. S. Geol. Surv. Water-Resour. Invest. 80-96, NTIS PB 81-167801 (1980).

(2) Wolery, T. J. : Calculation of Chemical Equibrium between Aqueous Solution and Minerals : The EQ3/6 Software Package, UCRL-52658 (1979).

(3) Bruno, J., et al. : Radionuclide solubilities to be used in SKB 91, SKB TR 92-13 (1992).

(4) SKI, Swedish Nuclear Power Inspectorate :SKI Project-90, SKI Technical Report 91:23 (1991).

(5) Vuorinen, U., et al. : Solubility and speciation calculations (EQ3/6) for the elements of importance in TVO-92, YJT-92-11 (1992).

(6) PNC, Power Reactor and Nuclear Fuel Development Co. : Technical Report on Research and Deveopment of Geological Disposal for High Level Radioactive Waste -H3 (in Japanese) PNC TN 1410 92-081 (1992).

(7) Curti, E. : Modelling bentonite pore waters for the Swiss high-level radioactive waste repository, PSI Bericht Nr.93-05 (1993).

(8) Berner, U. : Estimates of Solubility Limits for Safety Relevant Radionuclides, PSI Bericht Nr. 95-07 (1995).

(9) Yamaguchi, T. and Takeda, S. : Consideration on Thermodynamic Data for Predicting Solubility and Chemical Species of Elements in Groundwater :Part1: Tc, U, Am (in Japanese), JAERI-Data/Code 99-001 (1999).

(10) Wikberg, P., Alxelsen, K. and Fredlund, F. : Deep groundwater chemistry, SKB Technical Report 87-07.

(11) Wikberg, P. : Radionuclide sorption from the safety evaluation perspective, "Laboratory Eh simulations in relation to the redox conditions in natural granitic groundwaters", Nuclear Energy Agency, 217-234 (1992).

(12) SKB, Swedish Nuclear Fuel and Waste Management Co. : SKB91,"Final disposal of spent nuclear fuel. Importance of the bedrock for safety", SKB Technical Report TR 92-20 (1992).

(13) Mori, K. and Ikeda, K. : Investigation of Ground-water in Kamikita and Shimokita Districts, Aomori Prefecture (in Japanese), Monthly report of the Geological Survey, 15, 5 (1964).

(14) Noma, Y., Kino, Y. and Goto, H. : Ground Water in the Kuzuryu River Basin, Fukui Prefecture (in Japanese), Monthly report of the Geological Survey, 20, 12 (1969).

(15) Noma, Y.and Goto, H.:Groundwater in Ochigata Plain, Ishikawa Prefecture (in Japanese), Monthly Report of the Geological Survey, 21, 9 (1970).

(16) Murashita, T., Noma, Y., Kishi, K. and Ikeda, K. : Artesian Water in Hamamatsu City, Shizuoka Prefecture (in Japanese), Monthly Report of the Geological Survey, 13, 2 (1962).

(17) Kishi, K., Kanno, T. and Goto, H. : Investigation for Ground Water Resources in the

Northern Part of the Matsumoto Basin (in Japanese), Monthly Report of the Geological Survey, 17, 4 (1966).

(18) Ochiai, Y., Yamazaki, M., Harashima, H. and Takeda, S. : Natural Analogue Study of Tono Uranium Deposit in Japan, Report of the 3rd Meeting of CEC Natural Analogue Working Group, 126-138 (1988).

(19) Takahashi, S. and Ikeda, K. : On the Ground-water Resources in the Yamato Basin, Nara Prefecture (in Japanese), Monthly Report of the Geological Survey, 16, 7 (1965).

(20) Takahashi, S. and Goto, H. : Ground-water Resources for Industry in the Eastern Part of Chikushi Plain, Saga and Fukuoka Prefectures (in Japanese), Monthly Report of the Geological Survey, 17, 12 (1966).

(21) Snellman, M., et al. : Scientific Basis for Nuclear Waste Management X, "Laboratory and Modelling Studies of Sodium Bentonite Groundwater Interaction", Materials Research Society, 781-790 (1987).

(23) Atkinson, A. : The Time Dependance of pH within a Repository for Radioactive Waste Disposal, AERE-R11777 (1985).

(24) Berner, U. : A Thermodynamic Description of the Evolution of Pore Water Chemistry and Uranium Speciation during the Degradation of Cement, PSI-Bericht Nr. 62 (1990).

(25) Atkinson, A. and Hearne, J. A. : An assessment of the long-term durability of concrete in radioactive waste repositories, AERE-R 11465 (1984)

(26) Mihara, M., Iriya, K. et al. :Experimental and modelling studies on the interaction between cement paste with silica fume and distrilled water (in Japanese), Radioactive Waste Research, 3, 2 (1997)

(27) Silva, R. J. and Nitsche, H. : Actinide Enviromental Chemistry, Radiochimica Acta, 70/71, 377-396 (1995).

(28) Akimoto, T., Nakayama, S., Iida, Y. and Nagano, T. : Leachability of Bituminized Radioactive Waste : Literature Survey (in Japanese), JAERI-Review 99-002 (1999).

(29) IAEA: Bituminization of Radioactive Wastes, Technical Report Series No. 116, International Atomic Energy Agency, Vienna (1970).

(30) OECD/NEA : Chemical Thermodynamics Vol. 2, Chemical Thermodynamics of Americium, North-Holland (1995).

(31) Yamaguchi, T. and Nakayama, S. : Consideration on Thermodynamic Data for Am(III) in Aqueous Carbonate System (in Japanese), Radioactive Waste Research, 3, 1, 49-61 (1996).

(32) Lahr,H. and Knoch, W. : Bestimmung von Stabilitatskonstanten einiger Aktinidenkomplexe: II. Nitrat- und Chloridkomplexe von Uran, Neptunium, Plutonium und Americium (in German), Radiochimica Acta, 13 (1970).

(33) Brown, P.L. and Wanner, H. : Predicted formation constants using the unified theory of metal ion complexation, Paris: OECD Nuclear Energy Agency, (1987).

(34) Nitsche, H. : Basic research for assessment of geologic nuclear waste repositories: What

solubility and speciation studies of transuranium elements can tell us, MRS proc., vol.212 (1991).

(35) Puigdomenech, I. and Bruno, J. : Plutonium solubilities, SKB TR 91-04 (1991).

(36) Robert, J., Lemire, R. J. and Garisto, F. : The solubility of U, Np, Pu, Th and Tc in a geological disposal vault for used nuclear fuel, AECL-10009 (1989).

(37) Fuger, J., et al. : The Chemical Thermodynamics of Actinide Elements and Compounds Part12 : The ActinideAqueous Inorganic Complexes, IAEA,Vienna (1992).

(38) Kim, J.I., Lierse, C. and Baumgartener, F. : Plutonium chemistry, "Complexation of the Pu (IV) ion in carbonate-bicarbonate solutions", ACS Symposium Series, 216 (1983).

(39) Lierse, C. and Kim, J.I., Chemisches Verhalten von Plutonium in natuerlichen aquatischen Systemen:Hydrolyse (in German), Carbonatkomplexierung und Redoxreaktionen, RCM 02286, TU Muenchen, Munich, Germany (1986).

(40) Yamaguchi, T., Sakamoto, Y and Ohnuki, T. : Effect of the complexation on solubility of Pu(IV) in aqueous carbonate system, Radiochimica Acta 66/67, 9-14 (1994).

(41) Nitsche, H. and Silva, R. J. : Investigation of the Carbonate Complexation of Pu(IV) in Aqueous Solutions, Radiochimica Acta 72, 65-72 (1996).

(42) Tait, C. D., Ekberg, S. A., et al. : Plutonium Carbonate Speciation Changes as Measured in Dilute Solutions with Photoacounstic Spectroscopy, LA-12886-MS (1995).

(43) Eriksen, T. E., et al. : Solubility of the redox-sensitive radionuclides ^{99}Tc and ^{237}Np under reducing conditions in neutral to alkaline solutions.Effect of carbonate, SKB TR 93-18 (1993).

(44) Rard, J. A. : Critical review of the chemistry and thermodynamics of Tc and some of its inorganic compounds and aqueous species, UCRL-53440 (1983).

(45) Isherwood, D. : Application of the Ruthenium and Technetium Thermodynamic Data Base Used in the EQ3/6 Geochemical Codes, UCRL-53594 (1985).

(46) Puigdomenech, I. and Bruno, J. : A thermodynamic data base for Tc to calculate equilibrium solubilities at temperatures up to 300℃, SKB TR 95-09 (1995).

(47) Lemire, R. J. and Jobe, D. J..: Predicted behavior of technetium in a geological disposal vault for used nuclear fuel - Ramifications of a Recent Determination of the Henthalpy of Formation of TcO_2(cr) : Mat. Res. Soc. Symp. Proc., 412, 873-880 (1996).

(48) Kim, J. I. and Kanellakopulos, B. : Solubility products of plutonium(IV) oxide and hydroxide, Radiochimica Acta 48, 145-150 (1989).

(49) Denotkina, R.G., Moskvin, A.I. and Shevchenko, V.B. : The solubility product of plutonium(IV) hydrogen phosphate and its solubility in various acids, Russ. J. Inorg. Chem., 5, 387-389 (1960).

(50) Cowan, C.E., Jenne, E.A., Robertson, D.E., Nelson, D.M., Abel, K.H. : Transuranic chemical species in groundwater: Final Report, PNL-5263 (1985).

(51) Meyer, R. E., et al. : Solubilities of Tc(IV) Oxides, Radiochimica Acta 55, 11-18 (1991).

Appendix

Thermodynamics Data for Americium, Plutonium and Technetium

NOTATION

ΔG_f^0 : Standard Molar Gibbs energy of formation

$\log K^0$: Equilibrium Constant

Table A-1 Americium thermodynamic data, according to Yamaguchi,T. and Takeda, S. JAERI-Data/Code (1998).

species	ΔG_f^0 (kJ/mol)	reaction	log K⁰
Am(II)			
Am^{2+}	-376.8	$Am^{3+} + 0.5H_2O = Am^{2+} + H^+ + 0.25O_2(g)$	-38.9
Am(III)			
Am^{3+}	-598.7	master species	
$AmOH^{2+}$	-799.3	$Am^{3+} + H_2O = AmOH^{2+} + H^+$	-6.4
$Am(OH)_2^+$	-992.5	$Am^{3+} + 2H_2O = Am(OH)_2^+ + 2H^+$	-14.1
$Am(OH)_3^0$	-1163.4	$Am^{3+} + 3H_2O = Am(OH)_3^0 + 3H^+$	-25.7
$AmCO_3^+$	-1171.1	$Am^{3+} + CO_3^{2-} = AmCO_3^+$	7.8
$Am(CO_3)_2^-$	-1722.4	$Am^{3+} + 2CO_3^{2-} = Am(CO_3)_2^-$	11.9
$Am(CO_3)_3^{3-}$	-2269.2	$Am^{3+} + 3CO_3^{2-} = Am(CO_3)_3^{3-}$	15.2
$Am(OH)CO_3^0$	-1361.5	$Am^{3+} + H_2O + CO_3^{2-} = Am(OH)CO_3^0 + H^+$	-0.4
$Am(OH)_2CO_3^-$	-1550.0	$Am^{3+} + 2H_2O + CO_3^{2-} = Am(OH)_2CO_3^- + 2H^+$	-8.9
$AmOH(CO_3)_2^{2-}$	-1912.1	$Am^{3+} + H_2O + 2CO_3^{2-} = AmOH(CO_3)_2^{2-} + H^+$	3.6
$AmSO_4^+$	-1364.7	$Am^{3+} + SO_4^{2-} = AmSO_4^+$	3.85
$Am(SO_4)_2^-$	-2117.5	$Am^{3+} + 2SO_4^{2-} = Am(SO_4)_2^-$	5.40
$Am(SO_4)_3^{3-}$	-2859.2	$Am^{3+} + 3SO_4^{2-} = Am(SO_4)_3^{3-}$	5.0
$Am(SO_4)_4^{5-}$	-3597.5	$Am^{3+} + 4SO_4^{2-} = Am(SO_4)_4^{5-}$	4.0
$Am(SO_4)_5^{7-}$	-4329.0	$Am^{3+} + 5SO_4^{2-} = Am(SO_4)_5^{7-}$	1.8
$AmNH_3^{3+}$	-645.9	$Am^{3+} + NH_4^+ = AmNH_3^{3+} + H^+$	-5.6
$Am(NH_3)_2^{3+}$	-688.6	$Am^{3+} + 2NH_4^+ = Am(NH_3)_2^{3+} + 2H^+$	-12.1
$Am(NH_3)_3^{3+}$	-727.9	$Am^{3+} + 3NH_4^+ = Am(NH_3)_3^{3+} + 3H^+$	-19.1
$Am(NH_3)_4^{3+}$	-763.1	$Am^{3+} + 4NH_4^+ = Am(NH_3)_4^{3+} + 4H^+$	-26.8
$Am(NH_3)_5^{3+}$	-796.1	$Am^{3+} + 5NH_4^+ = Am(NH_3)_5^{3+} + 5H^+$	-35.0
$Am(NH_3)_6^{3+}$	-825.7	$Am^{3+} + 6NH_4^+ = Am(NH_3)_6^{3+} + 6H^+$	-43.7
AmN_3^{2+}	-260.0	$Am^{3+} + N_3^- = AmN_3^{2+}$	1.67
$AmNO_2^{2+}$		$Am^{3+} + NO_2^- = AmNO_2^{2+}$	2.10
$AmNO_3^{2+}$	-717.1	$Am^{3+} + NO_3^- = AmNO_3^{2+}$	1.33
$Am(NO_3)_2^+$	-826.6	$Am^{3+} + 2NO_3^- = Am(NO_3)_2^+$	1.1
$Am(NO_3)_3^0$	-933.4	$Am^{3+} + 3NO_3^- = Am(NO_3)_3^0$	0.4
$Am(NO_3)_4^-$	-1036.2	$Am^{3+} + 4NO_3^- = Am(NO_3)_4^-$	-1.0
$Am(NO_3)_5^{2-}$	-1136.1	$Am^{3+} + 5NO_3^- = Am(NO_3)_5^{2-}$	-2.9
$Am(NO_3)_6^{3-}$	-1232.1	$Am^{3+} + 6NO_3^- = Am(NO_3)_6^{3-}$	-5.5
AmF^{2+}	-899.6	$Am^{3+} + F^- = AmF^{2+}$	3.40
AmF_2^+	-1194.9	$Am^{3+} + 2F^- = AmF_2^+$	5.80
$AmCl^{2+}$	-735.9	$Am^{3+} + Cl^- = AmCl^{2+}$	1.05
$AmSCN^{2+}$	-513.4	$Am^{3+} + SCN^- = AmSCN^{2+}$	1.30
$AmH_2PO_4^{2+}$	-1753.0	$Am^{3+} + H_2PO_4^- = AmH_2PO_4^{2+}$	3.00
$Am(OH)_3(am)$	-1213.1	$Am^{3+} + 3H_2O = Am(OH)_3(am) + 3H^+$	-17.00
$Am(OH)_3(cr)$	-1223.4	$Am^{3+} + 3H_2O = Am(OH)_3(cr) + 3H^+$	-15.20
$Am_2O_3(cr)$	-1613.3	$2Am^{3+} + 3H_2O = Am_2O_3(cr) + 6H^+$	-51.8
$Am_2(CO_3)_3(cr)$	-2971.7	$Am^{3+} + 1.5CO_3^{2-} = 0.5Am_2(CO_3)_3(cr)$	16.7
$AmOHCO_3(cr)$	-1404.8	$Am^{3+} + OH^- + CO_3^{2-} = AmOHCO_3(cr)$	21.2
$AmF_3(cr)$	-1518.8	$Am^{3+} + 3F^- = AmF_3(cr)$	13.3
$AmCl_3(cr)$	-910.7	$Am^{3+} + 3Cl^- = AmCl_3(cr)$	-14.3
$Cs_2NaAmCl_6(cr)$	-2164.8	$Am^{3+} + 2Cs^+ + Na^+ + 6Cl^- = Cs_2NaAmCl_6(cr)$	-11.6
$AmOCl(cr)$	-902.5	$Am^{3+} + H_2O + Cl^- = AmOCl(cr) + 2H^+$	-11.3
$AmBr_3(cr)$	-786.5	$Am^{3+} + 3Br^- = AmBr_3(cr)$	-21.7
$AmOBr(cr)$	-861.3	$Am^{3+} + H_2O + Br^- = AmOBr(cr) + 2H^+$	-13.7
$AmI_3(cr)$	-613.3	$Am^{3+} + 3I^- = AmI_3(cr)$	-24.6
$AmPO_4(am,hydr)$		$Am^{3+} + PO_4^{3-} = AmPO_4(am,hydr)$	24.79
Am(IV)			
Am^{4+}	-346.4	$Am^{3+} + H^+ + 0.25O2(g) = Am^{4+} + 0.5H_2O$	-23.
$Am(CO_3)_5^{6-}$	-3210.2	$Am^{4+} + 5CO_3^{2-} = Am(CO_3)_5^{6-}$	39.4
$AmO_2(cr)$	-874.5	$Am^{4+} + 2H_2O = AmO_2(cr) + 4H^+$	9.4
$AmF_4(cr)$	-1616.8	$Am^{4+} + 4F^- = AmF_4(cr)$	25.3
Am(V)			
AmO_2^+	-739.8	$Am^{3+} + H_2O + 0.5O_2(g) = AmO_2^+ + 2H^+$	-16.8
Am(VI)			

AmO_2^{2+}	-585.8	$Am^{3+} + 0.5H_2O + 0.75O_2(g) = AmO_2^{2+} + H^+$	-23.0

other americium compounds

$AmH_2(cr)$	-134.7	$Am^{3+} + 2.5H_2O = AmH_2(cr) + 1.25O_2(g) + 3H^+$	-185.2
$Am_2C_3(cr)$	-156.1	$2Am^{3+} + 3CO_3^{2-} = Am_2C_3(cr) + 4.5O_2(g)$	-459.9

Table A-2 Plutonium thermodynamic data, according to Yamaguchi,T. and Takeda, S. JAERI-Data/Code (1998).

species	ΔG_f^0 (kJ/mol)	reaction	log K⁰
Pu(III)			
Pu³⁺	-579.1[1]	Pu⁴⁺ + 0.5H₂O = Pu³⁺ + H⁺ + 0.25O₂(g)	-3.8
PuOH²⁺	-770.3	Pu³⁺ + H₂O = PuOH²⁺ + H⁺	-8.0[2]
PuCO₃⁺	-1152.1	Pu³⁺ + CO₃²⁻ = PuCO₃⁺	7.9[3]
PuSO₄⁺	-1348.8	Pu³⁺ + SO₄²⁻ = PuSO₄⁺	4.5[4]
Pu(SO₄)₂⁻	-2105.3	Pu³⁺ + 2SO₄²⁻ = Pu(SO₄)₂⁻	6.7[4]
Pu(SO₄)₃³⁻	-2839.5	Pu³⁺ + 3SO₄²⁻ = Pu(SO₄)₃³⁻	4.98[5]
Pu(SO₄)₄⁵⁻	-3577.8	Pu³⁺ + 4SO₄²⁻ = Pu(SO₄)₄⁵⁻	3.97[5]
Pu(SO₄)₅⁷⁻	-4309.2	Pu³⁺ + 5SO₄²⁻ = Pu(SO₄)₅⁷⁻	1.77[5]
PuNH₃³⁺	-625.8	Pu³⁺ + NH₄⁺ = PuNH₃³⁺ + H⁺	-5.73[5]
Pu(NH₃)₂³⁺	-667.7	Pu³⁺ + 2NH₄⁺ = Pu(NH₃)₂³⁺ + 2H⁺	-12.30[5]
Pu(NH₃)₃³⁺	-705.6	Pu³⁺ + 3NH₄⁺ = Pu(NH₃)₃³⁺ + 3H⁺	-19.58[5]
Pu(NH₃)₄³⁺	-739.7	Pu³⁺ + 4NH₄⁺ = Pu(NH₃)₄³⁺ + 4H⁺	-27.53[5]
Pu(NH₃)₅³⁺	-770.1	Pu³⁺ + 5NH₄⁺ = Pu(NH₃)₅³⁺ + 5H⁺	-36.11[5]
Pu(NH₃)₆³⁺	-797.0	Pu³⁺ + 6NH₄⁺ = Pu(NH₃)₆³⁺ + 6H⁺	-45.31[5]
PuNO₃²⁺	-697.9	Pu³⁺ + NO₃⁻ = PuNO₃²⁺	1.41[6]
Pu(NO₃)₂⁺	-813.3	Pu³⁺ + 2NO₃⁻ = Pu(NO₃)₂⁺	2.22[6]
Pu(NO₃)₃⁰	-925.8	Pu³⁺ + 3NO₃⁻ = Pu(NO₃)₃⁰	2.52[6]
Pu(NO₃)₄⁻	-1013.9	Pu³⁺ + 4NO₃⁻ = Pu(NO₃)₄⁻	-1.48[5]
Pu(NO₃)₅²⁻	-1111.7	Pu³⁺ + 5NO₃⁻ = Pu(NO₃)₅²⁻	-3.75[5]
Pu(NO₃)₆³⁻	-1205.8	Pu³⁺ + 6NO₃⁻ = Pu(NO₃)₆³⁻	-6.67[5]
PuF²⁺	-880.0	Pu³⁺ + F⁻ = PuF²⁺	3.4[7]
PuF₂⁺	-1175.2	Pu³⁺ + 2F⁻ = PuF₂⁺	5.8[7]
PuCl²⁺	-717.7	Pu³⁺ + Cl⁻ = PuCl²⁺	1.3[4]
PuH₂PO₄²⁺	-1728.2	Pu³⁺ + H₂PO₄⁻ = PuH₂PO₄²⁺	2.1[6]
Pu(H₂PO₄)₂⁺	-2871.7	Pu³⁺ + 2H₂PO₄⁻ = Pu(H₂PO₄)₂⁺	3.2[6]
Pu(OH)₃(cr)	-1200.4	Pu³⁺ + 3H₂O = Pu(OH)₃(cr) + 3H⁺	-15.8[8]
Pu₂O₃(β)	-1580.0[9]	2Pu³⁺ + 3H₂O = Pu₂O₃(β) + 6H⁺	-50.7
PuOHCO₃(s)	-1385.3	Pu³⁺ + H₂O + CO₃²⁻ = PuOHCO₃(s) + H⁺	7.2[7]
Pu₂S₃(cr)	-979.0[10]	2Pu³⁺ + 3HS⁻ = Pu₂S₃(cr) + 3H⁺	-25.0
PuF₃(cr)	-1516.4[11]	Pu³⁺ + 3F⁻ = PuF₃(cr)	16.2
PuCl₃(cr)	-892.0[11]	Pu³⁺ + 3Cl⁻ = PuCl₃(cr)	-14.1
PuCl₃·6H₂O(s)	-2364.9[11]	Pu³⁺ + 3Cl⁻ + 6H₂O = PuCl₃·6H₂O(s)	-5.4
PuOCl(cr)	-882.0[11]	Pu³⁺ + Cl⁻ +H₂O = PuOCl(cr) + 2H⁺	-11.5
Pu(IV)			
Pu⁴⁺	-482.1[1]	master species	
PuOH³⁺	-715.9	Pu⁴⁺ + H₂O = PuOH³⁺ + H⁺	-0.58[2]
Pu(OH)₂²⁺	-942.0	Pu⁴⁺ + 2H₂O = Pu(OH)₂²⁺ + 2H⁺	-2.5[2]
Pu(OH)₃⁺	-1163.0	Pu⁴⁺ + 3H₂O = Pu(OH)₃⁺ + 3H⁺	-5.3[2]
Pu(OH)₄⁰	-1378.0	Pu⁴⁺ + 4H₂O = Pu(OH)₄⁰ + 4H⁺	-9.2[2]
PuCO₃²⁺	-1080.2	Pu⁴⁺ + CO₃²⁻ = PuCO₃²⁺	12.3[12]
Pu(CO₃)₂⁰	-1671.3	Pu⁴⁺ + 2CO₃²⁻ = Pu(CO₃)₂⁰	23.4[12]
Pu(CO₃)₃²⁻	-2237.2	Pu⁴⁺ + 3CO₃²⁻ = Pu(CO₃)₃²⁻	30.0[12]
Pu(CO₃)₄⁴⁻	-2781.1	Pu⁴⁺ + 4CO₃²⁻ = Pu(CO₃)₄⁴⁻	32.8[12]
Pu(CO₃)₅⁶⁻	-3315.2	Pu⁴⁺ + 5CO₃²⁻ = Pu(CO₃)₅⁶⁻	33.9[12]
Pu(OH)₂(CO₃)₂²⁻	-2125.5	Pu⁴⁺ + 2H₂O + 2CO₃²⁻ = Pu(OH)₂(CO₃)₂²⁻ + 2H⁺	19.9[13]
Pu(OH)₄(CO₃)₂⁴⁻	-2465.4	Pu⁴⁺ + 4H₂O + 2CO₃²⁻ = Pu(OH)₄(CO₃)₂⁴⁻ + 2H⁺	-3.7[13]
PuSO₄²⁺	-1268.8[4]	Pu⁴⁺ + SO₄²⁻ = PuSO₄²⁺	7.5
Pu(SO₄)₂⁰	-2036.7[4]	Pu⁴⁺ + 2SO₄²⁻ = Pu(SO₄)₂⁰	11.7
Pu(SO₄)₃²⁻	-2777.7	Pu⁴⁺ + 3SO₄²⁻ = Pu(SO₄)₃²⁻	11.14[5]
Pu(SO₄)₄⁴⁻	-3528.7	Pu⁴⁺ + 4SO₄²⁻ = Pu(SO₄)₄⁴⁻	12.37[5]
Pu(SO₄)₅⁶⁻	-4273.4	Pu⁴⁺ + 5SO₄²⁻ = Pu(SO₄)₅⁶⁻	12.50[5]
Pu(SO₄)₆⁸⁻	-5012.2	Pu⁴⁺ + 6SO₄²⁻ = Pu(SO₄)₆⁸⁻	11.58[5]
PuNH₃⁴⁺	-553.5	Pu⁴⁺ + NH₄⁺ = PuNH₃⁴⁺ + H⁺	-1.40[5]
Pu(NH₃)₂⁴⁺	-621.9	Pu⁴⁺ + 2NH₄⁺ = Pu(NH₃)₂⁴⁺ + 2H⁺	-3.33[5]
Pu(NH₃)₃⁴⁺	-687.8	Pu⁴⁺ + 3NH₄⁺ = Pu(NH₃)₃⁴⁺ + 3H⁺	-5.69[5]
Pu(NH₃)₄⁴⁺	-751.7	Pu⁴⁺ + 4NH₄⁺ = Pu(NH₃)₄⁴⁺ + 4H⁺	-8.41[5]
Pu(NH₃)₅⁴⁺	-813.7	Pu⁴⁺ + 5NH₄⁺ = Pu(NH₃)₅⁴⁺ + 5H⁺	-11.46[5]
Pu(NH₃)₆⁴⁺	-873.9	Pu⁴⁺ + 6NH₄⁺ = Pu(NH₃)₆⁴⁺ + 6H⁺	-14.82[5]
PuNO₃³⁺	-607.7	Pu⁴⁺ + NO₃⁻ = PuNO₃³⁺	2.6[4]
Pu(NO₃)₂²⁺	-722.8	Pu⁴⁺ + 2NO₃⁻ = Pu(NO₃)₂²⁺	3.36[3]

Species	ΔG	Reaction	log K
$Pu(NO_3)_3^+$	-834.8	$Pu^{4+} + 3NO_3^- = Pu(NO_3)_3^+$	3.56 [5]
$Pu(NO_3)_4^0$	-946.2	$Pu^{4+} + 4NO_3^- = Pu(NO_3)_4^0$	3.66 [5]
$Pu(NO_3)_5^-$	-1055.3	$Pu^{4+} + 5NO_3^- = Pu(NO_3)_5^-$	3.36 [5]
$Pu(NO_3)_6^{2-}$	-1162.4	$Pu^{4+} + 6NO_3^- = Pu(NO_3)_6^{2-}$	2.71 [5]
PuF^{3+}	-811.7 [4]	$Pu^{4+} + F^- = PuF^{3+}$	8.4
PuF_2^{2+}	-1135.5 [3]	$Pu^{4+} + 2F^- = PuF_2^{2+}$	15.8
$PuCl^{3+}$	-622.8	$Pu^{4+} + Cl^- = PuCl^{3+}$	1.67 [11]
$PuCl_2^{2+}$	-756.8	$Pu^{4+} + 2Cl^- = PuCl_2^{2+}$	2.16 [3]
$PuH_2PO_4^{3+}$	-1647.5 [6]	$Pu^{4+} + H_2PO_4^- = PuH_2PO_4^{3+}$	4.95
$Pu(H_2PO_4)_2^{2+}$	-2804.0 [6]	$Pu^{4+} + 2H_2PO_4^- = Pu(H_2PO_4)_2^{2+}$	8.35
$Pu(H_2PO_4)_4^0$	-5110.4 [6]	$Pu^{4+} + 4H_2PO_4^- = Pu(H_2PO_4)_4^0$	14.0
$PuHPO_4^{2+}$	-1652.3	$Pu^{4+} + HPO_4^{2-} = PuHPO_4^{2+}$	13.0 [14]
$Pu(HPO_4)_2^0$	-2811.2	$Pu^{4+} + 2HPO_4^{2-} = Pu(HPO_4)_2^0$	24.0 [14]
$Pu(HPO_4)_3^{2-}$	-3958.6	$Pu^{4+} + 3HPO_4^{2-} = Pu(HPO_4)_3^{2-}$	33.0 [14]
$Pu(HPO_4)_4^{4-}$	-5111.7	$Pu^{4+} + 4HPO_4^{2-} = Pu(HPO_4)_4^{4-}$	43.0 [14]
$Pu(OH)_4(am)$	-1441.0	$Pu^{4+} + 4H_2O = Pu(OH)_4(am) + 4H^+$	1.85 [15]
$PuO_2(cr)$	-1001.2	$Pu^{4+} + 2H_2O = PuO_2(cr) + 4H^+$	7.8 [15]
$Pu(SO_4)_2(cr)$	-2012.9 [10]	$Pu^{4+} + 2SO_4^{2-} = Pu(SO_4)_2(cr)$	7.5
$PuF_4(cr)$	-1752.9 [11]	$Pu^{4+} + 4F^- = PuF_4(cr)$	25.4
$Pu(HPO_4)_2(s)$	-2834.0	$Pu^{4+} + 2HPO_4^{2-} = Pu(HPO_4)_2(s)$	28.0 [16]

Pu(V)

Species	ΔG	Reaction	log K
PuO_2^+	-850.0 [1]	$Pu^{4+} + 1.5H_2O + 0.25O_2(g) = PuO_2^+ + 3H^+$	2.1
PuO_2OH^0	-1031.3	$PuO_2^+ + H_2O = PuO_2OH^0 + H^+$	-9.7 [17]
$PuO_2CO_3^-$	-1407.1	$PuO_2^+ + CO_3^{2-} = PuO_2CO_3^-$	5.12 [17]
$PuO_2SO_4^-$	-1602.0	$PuO_2^+ + SO_4^{2-} = PuO_2SO_4^-$	1.41 [5]
$PuO_2(SO_4)_2^{3-}$	-2345.0	$PuO_2^+ + 2SO_4^{2-} = PuO_2(SO_4)_2^{3-}$	1.23 [5]
$PuO_2(SO_4)_3^{5-}$	-3080.3	$PuO_2^+ + 3SO_4^{2-} = PuO_2(SO_4)_3^{5-}$	-0.30 [5]
$PuO_2(SO_4)_4^{7-}$	-3808.4	$PuO_2^+ + 4SO_4^{2-} = PuO_2(SO_4)_4^{7-}$	-3.08 [5]
$PuO_2NH_3^+$	-879.2	$PuO_2^+ + NH_4^+ = PuO_2NH_3^+ + H^+$	-8.79 [5]
$PuO_2(NH_3)_2^+$	-904.5	$PuO_2^+ + 2NH_4^+ = PuO_2(NH_3)_2^+ + 2H^+$	-18.27 [5]
$PuO_2(NH_3)_3^+$	-926.3	$PuO_2^+ + 3NH_4^+ = PuO_2(NH_3)_3^+ + 3H^+$	-28.36 [5]
$PuO_2(NH_3)_4^+$	-945.1	$PuO_2^+ + 4NH_4^+ = PuO_2(NH_3)_4^+ + 4H^+$	-38.98 [5]
$PuO_2(NH_3)_5^+$	-961.0	$PuO_2^+ + 5NH_4^+ = PuO_2(NH_3)_5^+ + 5H^+$	-50.11 [5]
$PuO_2NO_3^0$	-961.9	$PuO_2^+ + NO_3^- = PuO_2NO_3^0$	0.19 [5]
$PuO_2(NO_3)_2^-$	-1068.2	$PuO_2^+ + 2NO_3^- = PuO_2(NO_3)_2^-$	-0.59 [5]
$PuO_2(NO_3)_3^{2-}$	-1170.6	$PuO_2^+ + 3NO_3^- = PuO_2(NO_3)_3^{2-}$	-2.07 [5]
$PuO_2(NO_3)_4^{3-}$	-1269.5	$PuO_2^+ + 4NO_3^- = PuO_2(NO_3)_4^{3-}$	-4.16 [5]
$PuO_2(NO_3)_5^{4-}$	-1365.1	$PuO_2^+ + 5NO_3^- = PuO_2(NO_3)_5^{4-}$	-6.81 [5]
$PuO_2OH(s)$	-1060.1	$PuO_2^+ + H_2O = PuO_2OH(s) + H^+$	-4.7 [18]

Pu(VI)

Species	ΔG	Reaction	log K
PuO_2^{2+}	-756.0 [1]	$Pu^{4+} + H_2O + 0.5O_2(g) = PuO_2^{2+} + 2H^+$	6.45
PuO_2OH^+	-961.9	$PuO_2^{2+} + H_2O = PuO_2OH^+ + H^+$	-5.5 [19]
$(PuO_2)_2(OH)_2^{2+}$	-1941.0	$2PuO_2^{2+} + 2H_2O = (PuO_2)_2(OH)_2^{2+} + 2H^+$	-7.9 [2]
$(PuO_2)_3(OH)_5^+$	-3333.0	$3PuO_2^{2+} + 5H_2O = (PuO_2)_3(OH)_5^+ + 5H^+$	-21.1 [2]
$PuO_2(OH)_2^0$	-1154.1	$PuO_2^{2+} + 2H_2O = PuO_2(OH)_2^0 + 2H^+$	-13.3 [19]
$PuO_2(OH)_3^-$	-1336.6	$PuO_2^{2+} + 3H_2O = PuO_2(OH)_3^- + 3H^+$	-22.9 [20]
$PuO_2CO_3^0$	-1336.5	$PuO_2^{2+} + CO_3^{2-} = PuO_2CO_3^0$	9.2 [21]
$PuO_2(CO_3)_2^{2-}$	-1896.3	$PuO_2^{2+} + 2CO_3^{2-} = PuO_2(CO_3)_2^{2-}$	14.8 [21]
$PuO_2(CO_3)_3^{4-}$	-2439.1	$PuO_2^{2+} + 3CO_3^{2-} = PuO_2(CO_3)_3^{4-}$	17.4 [21]
$PuO_2SO_4^0$	-1519.3	$PuO_2^{2+} + SO_4^{2-} = PuO_2SO_4^0$	3.37 [22]
$PuO_2(SO_4)_2^{2-}$	-2265.2	$PuO_2^{2+} + 2SO_4^{2-} = PuO_2(SO_4)_2^{2-}$	3.71 [5]
$PuO_2(SO_4)_3^{4-}$	-3009.1	$PuO_2^{2+} + 3SO_4^{2-} = PuO_2(SO_4)_3^{4-}$	3.69 [5]
$PuO_2(SO_4)_4^{6-}$	-3747.0	$PuO_2^{2+} + 4SO_4^{2-} = PuO_2(SO_4)_4^{6-}$	2.62 [5]
$PuO_2(SO_4)_5^{8-}$	-4479.1	$PuO_2^{2+} + 5SO_4^{2-} = PuO_2(SO_4)_5^{8-}$	0.54 [5]
$PuO_2NH_3^{2+}$	-804.5	$PuO_2^{2+} + NH_4^+ = PuO_2NH_3^{2+} + H^+$	-5.41 [5]
$PuO_2(NH_3)_2^{2+}$	-850.4	$PuO_2^{2+} + 2NH_4^+ = PuO_2(NH_3)_2^{2+} + 2H^+$	-11.28 [5]
$PuO_2(NH_3)_3^{2+}$	-894.3	$PuO_2^{2+} + 3NH_4^+ = PuO_2(NH_3)_3^{2+} + 3H^+$	-17.51 [5]
$PuO_2(NH_3)_4^{2+}$	-936.4	$PuO_2^{2+} + 4NH_4^+ = PuO_2(NH_3)_4^{2+} + 4H^+$	-24.04 [5]
$PuO_2(NH_3)_5^{2+}$	-977.1	$PuO_2^{2+} + 5NH_4^+ = PuO_2(NH_3)_5^{2+} + 5H^+$	-30.83 [5]
$PuO_2NO_3^+$	-870.3	$PuO_2^{2+} + NO_3^- = PuO_2NO_3^+$	0.62 [5]
$PuO_2(NO_3)_2^0$	-980.4	$PuO_2^{2+} + 2NO_3^- = PuO_2(NO_3)_2^0$	0.49 [5]
$PuO_2(NO_3)_3^-$	-1087.7	$PuO_2^{2+} + 3NO_3^- = PuO_2(NO_3)_3^-$	-0.13 [5]
$PuO_2(NO_3)_4^{2-}$	-1192.7	$PuO_2^{2+} + 4NO_3^- = PuO_2(NO_3)_4^{2-}$	-1.14 [5]
$PuO_2(NO_3)_5^{3-}$	-1295.8	$PuO_2^{2+} + 5NO_3^- = PuO_2(NO_3)_5^{3-}$	-2.49 [5]
PuO_2F^+	-1063.6	$PuO_2^{2+} + F^- = PuO_2F_3^+$	4.6 [4]
$PuO_2F_2^0$	-1366.1	$PuO_2^{2+} + 2F^- = PuO_2F_2^0$	8.2 [4]

$PuO_2F_3^-$	-1656.6	$PuO_2^{2+} + 3F^- = PuO_2F_3^-$	9.8[4]
PuO_2Cl^+	-887.6	$PuO_2^{2+} + Cl^- = PuO_2Cl^+$	0.068[6]
$PuO_2Cl_2^0$	-1017.4	$PuO_2^{2+} + 2Cl^- = PuO_2Cl_2^0$	-0.18[3]
$PuO_2H_2PO_4^+$	-1915.6	$PuO_2^{2+} + H_2PO_4^- = PuO_2H_2PO_4^+$	3.9[16]
$PuO_2(OH)_2(s)$	-1205.3	$PuO_2^{2+} + 2H_2O = PuO_2(OH)_2(s) + 2H^+$	-4.4[23]
$PuO_2CO_3(s)$	-1368.7	$PuO_2^{2+} + CO_3^{2-} = PuO_2CO_3(s)$	14.8[24]
$PuO_2HPO_4(s)$	-1926.3	$PuO_2^{2+} + HPO_4^{2-} = PuO_2HPO_4(s)$	13.0[16]
$(UO_2)_2PuO_2(CO_3)_6^{6-}$	see uranium thermodynamic data		

plutonium hydride

$PuH_2(cr)$	-130.0[25]	$Pu^{4+} + 3H_2O = PuH_2(cr) + 4H^+ + 1.5O_2(g)$	-186.3

[1] Fuger, J. and Oetting, F. L., "The Chemical Thermodynamics of Actinide Elements and Compounds, Part 2: The Actinide Aqueous Ions", IAEA, Vienna (1976).
[2] Lemire, R. J. and Tremaine, P. R., J. Chem. Eng. Data 25, 361 (1980).
[3] Nitsche, H., Mat. Res. Soc. Symp. Proc., vol. 212, pp. 517 (1991).
[4] Fuger, J., et al., "The Chemical Thermodynamics of Actinides Elements and Compounds, Part 12: The Actinide Aqueous Inorganic Complexes", IAEA, Vienna (1992).
[5] Brown, P.L. and Wanner, H. "Predicted formation constants using the unified theory of metal ion complexation", OECD Nuclear Energy Agency, Paris, 102p (1987).
[6] Cowan, C. E., et al., PNL-5263 (1985).
[7] Silva, R. J., et al., "Chemical Thermodynamics of Americium", Elsevier, Amsterdam, 374p (1995).
[8] Felmy, A. R. and Rai, D., Radiochim. Acta 48, 29 (1989).
[9] Morss, L. R., "Thermodynamic Properties: The shemistry of the actinide elements, actinide aqueous ions" Vol. 2, London, New York, pp.1278-1360 (1986).
[10] Cordfunke, E. H. P. and O'Hare, P. A. G., "The Chemical Thermodynamics of Actinide Elements and Compounds Part 3: Miscellaneous Actinide Compounds", IAEA, Vienna (1978).
[11] Fuger, J., et al. "The chemical thermodynamics of actinide elements and compounds Part 8: The actinide halides", IAEA, Vienna (1983).
[12] Nitsche, H. and Silva, R. J., Radiochim. Acta 72, 65 (1996).
[13] Yamaguchi, T., et al., Radiochim. Acta 66/67, 9 (1994).
[14] Denotkina, R. G., et al., Russ. J. Inorg. Chem. 5, 387 (1960).
[15] Kim, J. I. and Kanellakopulos, B. Radiochim. Acta 48, 145 (1989).
[16] Denotkina, R. G. and Shevchenko, V. B., Russ. J. Inorg. Chem. 12, 1237 (1967).
[17] Bennett, D. A. and Hoffman, D., Radiochim. Acta 56, 15 (1992).
[18] Rai, D. and Serne, R. J., J. Environ. Qual. 6, 89 (1977).
[19] Pashalidis, I. and Kim, J. I., Radiochim. Acta 68, 99 (1995).
[20] Puigdomenech, I. and Bruno, J., SKB TR 91-04 (1991).
[21] Robouch, P. and Vitorge, P., Inorganica Chimica Acta 140, 239 (1987).
[22] Patil, S. K. and Ramarkishna, V. V., J. Inorg. Nucl. Chem. 38, 1075 (1976).
[23] Grenthe, I. and Wanner, H., Guidlines for the extrapolation to zero ionic strength code, NEA-TDB-2.1, F-91191, Gif-sur-Yvette, France (1989).
[24] Pashalidis, W., et al., Radiochim. Acta 61, 141 (1993).
[25] Flotow, H. E., et al., "The chemical thermodynamics of actinide elements and compounds Part 9: The actinide halides", IAEA, Vienna (1984).

Table A-3 Technetium thermodynamic data, according to Yamaguchi,T. and Takeda, S. JAERI-Data/Code (1998).

species	ΔG_f^0, (kJ/mol)	reaction	log K^0
Tc(II)			
Tc^{2+}	+77.0	$TcO_4^- + 3H^+ = Tc^{2+} + 1.5H_2O + 1.25O_2(g)$	-62.9
Tc(III)			
Tc^{3+}	+88.0	$TcO_4^- + 4H^+ = Tc^{3+} + 2H_2O + O_2(g)$	-44.0
$Tc(OH)Cl_3^-$	-554.2	$Tc^{3+} + OH^- + 3Cl^- = Tc(OH)Cl_3^-$	16.0
$Tc(OH)_2(CO_3)_2^{3-}$	-1447.1	$Tc^{3+} + 2OH^- + 2CO_3^{2-} = Tc(OH)_2(CO_3)_2^{3-}$	28.9
Tc(IV)			
TcO^{2+}	-118.3	$TcO_4^- + 3H^+ = TcO^{2+} + 1.5H_2O + 0.75O_2$	-28.6
$TcO(OH)^+$	-349.0	$TcO^{2+} + H_2O = TcO(OH)^+ + H^+$	-1.13
$TcO(OH)_2^0$	-569.2	$TcO^{2+} + 2H_2O = TcO(OH)_2^0 + 2H^+$	-4.1
$[TcO(OH)_2]_2^0$	-1175.5	$2TcO^{2+} + 4H_2O = [TcO(OH)_2]_2^0 + 4H^+$	-1.7
$TcO(OH)_3^-$	-744.2	$TcO^{2+} + 3H_2O = TcO(OH)_3^- + 3H^+$	-15.0
$Tc(OH)_2CO_3^0$	-970.4	$TcO^{2+} + H_2O + CO_3^{2-} = Tc(OH)_2CO_3^0$	15.3
$Tc(OH)_3CO_3^-$	-1144.7	$TcO^{2+} + 2H_2O + 2CO_3^{2-} = Tc(OH)_3CO_3^- + H^+$	3.0
$TcOH(CO_3)_2^-$	-1319.1	$TcO^{2+} + H^+ + 2CO_3^{2-} = TcOH(CO_3)_2^-$	25.4
$TcCl_5^-$	-540.7	$TcO^{2+} + 2H^+ + 5Cl^- = TcCl_5^- + H_2O$	0.6
$TcCl_6^{2-}$	-671.9	$TcO^{2+} + 2H^+ + 6Cl^- = TcCl_6^{2-} + H_2O$	0.6
$TcONO_3^+$	-235.4	$TcO^{2+} + NO_3^- = TcONO_3^+$	1.1
$TcO(NO_3)_2^0$	-347.3	$TcO^{2+} + 2NO_3^- = TcO(NO_3)_2^0$	1.3
$TcO(NO_3)_3^-$	-455.8	$TcO^{2+} + 3NO_3^- = TcO(NO_3)_3^-$	0.9
$TcO(NO_3)_4^{2-}$	-560.9	$TcO^{2+} + 4NO_3^- = TcO(NO_3)_4^{2-}$	-0.1
$TcO(NO_3)_5^{3-}$	-663.7	$TcO^{2+} + 5NO_3^- = TcO(NO_3)_5^{3-}$	-1.5
$TcONH_3^{2+}$	-186.1	$TcO^{2+} + NH_3 = TcONH_3^{2+}$	7.2
$TcO(NH_3)_2^{2+}$	-249.9	$TcO^{2+} + 2NH_3 = TcO(NH_3)_2^{2+}$	13.7
$TcO(NH_3)_3^{2+}$	-311.4	$TcO^{2+} + 3NH_3 = TcO(NH_3)_3^{2+}$	19.8
$TcO(NH_3)_4^{2+}$	-370.1	$TcO^{2+} + 4NH_3 = TcO(NH_3)_4^{2+}$	25.4
$TcO(NH_3)_5^{2+}$	-425.9	$TcO^{2+} + 5NH_3 = TcO(NH_3)_5^{2+}$	30.5
$TcOSO_4^0$	-882.8	$TcO^{2+} + SO_4^{2-} = TcOSO_4^0$	3.6
$TcO(SO_4)_2^{2-}$	-1638.3	$TcO^{2+} + 2SO_4^{2-} = TcO(SO_4)_2^{2-}$	5.6
$TcO(SO_4)_3^{4-}$	-2386.8	$TcO^{2+} + 3SO_4^{2-} = TcO(SO_4)_3^{4-}$	6.4
$TcO(SO_4)_4^{6-}$	-3128.0	$TcO^{2+} + 4SO_4^{2-} = TcO(SO_4)_4^{6-}$	5.9
$TcO(SO_4)_5^{8-}$	-3862.3	$TcO^{2+} + 5SO_4^{2-} = TcO(SO_4)_5^{8-}$	4.2
$TcO_2(cr)$	-404	$TcO^{2+} + H_2O = TcO_2(cr) + 2H^+$	8.5
$TcO_2 \cdot 2H_2O(s)$	-853.7	$TcO^{2+} + 3H_2O = TcO_2 \cdot 2H_2O(s) + 2H^+$	4.2
Tc(V)			
TcO_4^{3-}	-521.5	$TcO_4^- + H_2O = TcO_4^{3-} + 2H^+ + 0.5O_2(g)$	-61.9
$TcOCl_4^-$	-601.5	$TcO_4^{3-} + 6H^+ + 4Cl^- = TcOCl_4^- + 3H_2O$	46.7
$TcOCl_5^{2-}$	-702.5	$TcO_4^{3-} + 6H^+ + 5Cl^- = TcOCl_5^{2-} + 3H_2O$	41.4
$TcO_2Cl_4^{3-}$	-791.8	$TcO_4^{3-} + 4H^+ + 4Cl^- = TcO_2Cl_4^{3-} + 2H_2O$	38.5
Tc(VI)			
TcO_4^{2-}	-578.6	$TcO_4^- + 0.5H_2O = TcO_4^{2-} + H^+ + 0.25O_2(g)$	-31.1
$HTcO_4^-$	-628.3	$TcO_4^{2-} + H^+ = HTcO_4^-$	8.7
$H_2TcO_4^0$	-630.0	$TcO_4^{2-} + 2H^+ = H_2TcO_4^0$	9.0
Tc(VII)			
TcO_4^-	-637.4	master species	
$HTcO_4^0$	-638.0	$TcO_4^- + H^+ = HTcO_4^0$	-0.1
$HTcO_4(s)$	-589.8	$TcO_4^- + H^+ = HTcO_4(s)$	-8.3
$Tc_2O_7(cr)$	-935.6	$2TcO_4^- + 2H^+ = Tc_2O_7(cr) + H_2O$	-17.9
$NaTcO_4(s)$	-890.6	$TcO_4^- + Na^+ = NaTcO_4(s)$	-1.54
$KTcO_4(s)$	-933.0	$TcO_4^- + K^+ = KTcO_4(s)$	2.29