

Uranium (VI) speciation diagrams in the $\text{UO}_2^{2+}/\text{CO}_3^{2-}/\text{H}_2\text{O}$ system at 25°C

A. Krestou, D. Panias*

*National Technical University of Athens (NTUA), School of Mining and Metallurgical Engineering,
Section of Metallurgy and Materials Technology, Laboratory of Metallurgy,
9, Heroon Polytechniou St., Zografou Campus, 15780 Athens, Greece*

Received 16 December 2003; accepted 15 March 2004

ABSTRACT

Uranium is a toxic heavy metal that occurs naturally. Exploitation processes together with the utilization of the ^{235}U isotope in the nuclear industry produce huge amounts of wastes that are transferred through aqueous phases to the food chain. The kind of U(VI) species that are present under various conditions in an aqueous phase is the dominant parameter for the designing and application of the appropriate treatment technology. Consequently, the speciation of uranium in aqueous systems under several environmental conditions is of great importance for the protection of the environment and of human health. In the present paper the U(VI) aqueous speciation will be studied in the absence as well as in the presence of the CO_3^{2-} ligand under variable conditions such as ionic strength and total uranium (VI) concentration. In the case where the CO_3^{2-} ligand is present the simulation was performed in open to the atmosphere and closed systems. The speciation diagrams show that in aqueous solutions and pH values lower than about 3, uranium (VI) is present exclusively in the form of the uranyl cation, UO_6^{2+} . In systems that are free of carbonates, an increase of the solution pH favors the formation of positively charged hydroxo-uranium (VI) complexes that are transformed to negatively charged ones with a further pH increase. The same trend in the uranium (VI) aqueous species transformation is followed in open to the atmosphere systems, in which an increase of the solution pH up to about 8 causes the transformation of the uranyl ion to hydroxo-uranium complexes. However, in strongly alkaline conditions the concentration of carbonaceous complexing agents is higher than that of the hydroxide ion and therefore carbonato-uranyl species are formed. In systems that are closed to the atmosphere and contain constant amounts of dissolved carbonates, the transformation sequence of uranium (VI) species with increasing pH includes the formation of carbonato-uranium complexes in the low acidic and neutral region and finally the transition to hydroxo-uranium complexes in the alkaline pH region. © 2004 SDU. All rights reserved.

Keywords: Uranium; Aqueous speciation; Carbonato complexes

1. INTRODUCTION

Uranium is one of the heaviest naturally occurring elements. It belongs to the chemical series of actinides and thus is a radioactive element. Uranium comes essentially in three isotopic forms: ^{238}U , ^{235}U and ^{234}U . Naturally occurring uranium contains 99.27% ^{238}U , 0.72% ^{235}U and traces of ^{234}U . The isotope ^{235}U is of considerable significance to both nuclear facilities and military purposes because it is the only existing isotope in nature to any appreciable extent that is fissionable by thermal neutrons. The isotope ^{238}U is also important because it absorbs neutrons to produce a radioactive isotope that subsequently decays to the ^{239}Pu isotope, which is also fissionable by thermal neutrons (Lee, 1991).

Uranium vanadates such as carnotite $\text{K}_2(\text{UO}_2)_2(\text{VO}_4)_2 \cdot 3\text{H}_2\text{O}$ constitute the main ore of uranium. It is mined also as oxide ores, the most important of them being uraninite and pitchblende. The extraction of uranium from ores is a complex process (Lee, 1991). Uranium-bearing ores contain typically 0.05-0.2% of U_3O_8 , so 1 tonne of ore yields about 0.5-2kg of U_3O_8 . In order to produce uranium metal, uranium-bearing ores must be concentrated using a flotation method. The concentrate is roasted in air and leached with sulphuric acid in the presence of an oxidizing agent such as MnO_2 to ensure conversion to hexavalent uranium. Then, U(VI) is precipitated from the pregnant solution as sodium diuranate $\text{Na}_2\text{U}_2\text{O}_7$, a bright yellow

* Corresponding author. E-mail: panias@metal.ntua.gr

solid called yellowcake, which is further purified in order to produce uranium metal rods. The use of uranium as fuel for peaceful or military purposes requires the enrichment of metal in the fissionable isotope ^{235}U . Fuel is usually enriched to a reactor grade of 3.2-3.6% of ^{235}U for use in nuclear power stations or to a weapon grade that contains higher than 90% ^{235}U for use in weapons production and as a fuel in nuclear powered submarines. The separation of ^{238}U and ^{235}U isotopes and the enrichment of uranium in the ^{235}U isotope can be performed with four methods: thermal diffusion, gaseous diffusion, electromagnetic separation and using a gas centrifuge. The last one is becoming increasingly important using the different rates of diffusion of gaseous $^{238}\text{UF}_6$ and $^{235}\text{UF}_6$. This process does not only produce the enriched metal, but also a waste stream depleted in ^{235}U , often called depleted uranium, that typically contains less than 0.3% ^{235}U .

The life cycle of uranium for peaceful purposes involves the following typical processes: Ore mining, ore processing, extraction of metal, enrichment of metal and nuclear fission in power stations. All the above processes are potentially hazardous because they produce huge amounts of radioactive wastes that are stored in the ground or in geological formations. The only conceivable transport medium for these hazardous materials is the aqueous phase. Rainwater can leach the hazardous wastes and the leachates can penetrate the soil and pollute the surface, ground and underground waters posing a serious environmental threat to the surrounding area. In Europe alone, fourteen countries face the problem of contamination caused by uranium, which represents a particularly serious danger where drinking water resources might be affected (PEREBAR, 1999; Combkoto *et al.*, 2001; Veselic *et al.*, 2001).

Uranium presents both chemical and radiological hazards and is very dangerous for the human health. It is reported (Rostker, 1998; Zamora *et al.*, 1998) that the long-term ingestion of uranium by humans may produce interference with kidney function at the elevated levels of uranium found in some groundwater supplies. The RAND (Research and Development) review on radiological and toxic effects of uranium (Zajic, 1999) puts the overall maximum permissible concentration of uranium metal in the kidney at 3mg/kg of kidney. Soluble uranium, which is absorbed in the blood, is eliminated rapidly through the kidney in urine. About 67% is excreted within the first day without being deposited in any organ. Approximately 11% is initially deposited in the kidney and excreted with a 15-day half-life. Most of the remaining 22% is deposited mainly in the bone and in other organs and tissues. The observed effects may represent a manifestation of sub-clinical toxicity, which will not necessarily lead to kidney failure or overt illness. It may however, be the first step in a series of progressive or irreversible renal injury results from the chronic intake of elevated levels of uranium over time.

Due to its hazardous nature, soluble uranium has to be removed from surface, ground and underground waters to a value set by local authorities. U.S. Environmental Protection Agency (EPA) standards set the values of uranium contamination at 44 $\mu\text{g}/\text{l}$ for groundwater and 20 $\mu\text{g}/\text{l}$ for drinking water (Zajic, 1999). The development of uranium attenuation processes is strongly dependent on the chemical behavior of uranium in aqueous systems. Particularly, the determination of the acting species of uranium in aqueous systems under various environmental conditions is of primary importance for the understanding of uranium transport mechanism from the waste towards aqueous phase as well as the uranium attenuation mechanism from polluted waters. This information is provided by speciation calculations using chemical thermodynamic data.

The present study focuses on the construction of uranium speciation diagrams under various total uranium concentrations, ionic strengths and pH of aqueous solutions. As the U(VI) solubility is affected by common ligands such as carbonates, the uranium speciation diagrams are constructed both in the absence and the presence of carbonates in solution. In the latter case, uranium speciation diagrams are constructed under environmental conditions at equilibrium with the atmospheric CO_2 as well as in closed systems in order to simulate the conditions applied in the natural systems.

2. EQUILIBRIUM AND MASS BALANCE CALCULATIONS

2.1. Description of the $\text{UO}_2^{2+}/\text{CO}_3^{2-}/\text{H}_2\text{O}$ system

In order to determine the species present in the $\text{UO}_2^{2+}/\text{CO}_3^{2-}/\text{H}_2\text{O}$ system and construct the corresponding speciation diagrams, four general steps were followed.

- 1) Establishment of the nature of all the species present in the solution.
- 2) Determination and evaluation of the formation equilibrium constants of the various species at various ionic strengths. A bibliographic (Grenthe *et al.*, 1992; Gabriel *et al.*, 1998) and computer aided database (IUPAC) search was conducted in order to find reliable thermodynamic data at 25°C for the system studied. The most reliable source for thermodynamic data concerning uranium was the book from Grenthe *et al.*, 1992, and it is from this book that the majority of the data for this will be referenced from. Ionic strength corrections at values below 0.31M for reactions containing only ionic species were performed using the Davies equation (IUPAC, 1997; Butler, 1998):

$$\log \beta_n = \log \beta_n^0 + A \Delta z^2 \left(\frac{\sqrt{I}}{\sqrt{I} + 1} - 0.31I \right) \quad (1)$$

where,

β_n , is the concentration equilibrium constant at ionic strength I

β_n^0 , is the concentration equilibrium constant at zero ionic strength

A, is a function of the ambient temperature and the dielectric constant of water (at 1atm and 25°C: A = 0.511)

Δz^2 , is the difference between the sum of the squared product ion charges and reactant ion charges ($\Delta z^2 = \sum z^2(\text{product})_i - \sum z^2(\text{reactant})_j$)

and I, is the ionic strength in molarity scale.

- 3) Determination of mass balance relations and establishment of the total concentration of each component in the solution, so that there are as many independent equations as unknowns.
- 4) Estimation of all *n* unknowns from the system of the *n* simultaneous equations.

2.1.1. Hydroxo-U(VI) complex ions

Hexavalent uranium, U(VI), is present in aqueous solutions in the form of the uranyl ion, UO_2^{2+} , as well as in the form of mononuclear and polynuclear hydroxo- complexes with the general form $(\text{UO}_2)_m(\text{OH})_n^{2m-n}$. These species along with the corresponding thermodynamic data are listed in Table 1.

Table 1

Formation constants at 25°C according to the general equilibria, $m\text{UO}_2^{2+} + n\text{H}_2\text{O}(\text{l}) \rightleftharpoons (\text{UO}_2)_m(\text{OH})_n^{2m-n} + n\text{H}^+$

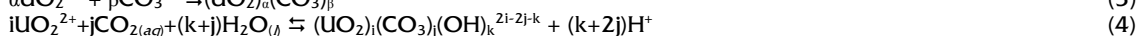
Species (m, n)	Ionic strength I (M)	Formation constant values	Reference
(1, 1)	0	$\beta^0_1 = -5.20$	Grenthe, 1992
(1, 2)	0.1	$\beta_{(1,2)} = -10.61$	Grenthe, 1992; IUPAC, 1997
(1, 3)	0	$\beta^0_{(1,3)} = -19.20$	Grenthe, 1992
(1, 4)	0	$\beta^0_{(1,4)} = -33.00$	Grenthe, 1992
(2, 1)	0	$\beta^0_{(2,1)} = -2.70$	Grenthe, 1992
(2, 2)	0	$\beta^0_{(2,2)} = -5.62$	Grenthe, 1992
(3, 4)	0	$\beta^0_{(3,4)} = -11.90$	Grenthe, 1992
(3, 5)	0	$\beta^0_{(3,5)} = -15.55$	Grenthe, 1992
(3, 7)	0	$\beta^0_{(3,7)} = -31.00$	Grenthe, 1992
(3, 8)	0.1	$\beta_{(3,8)} = -37.65$	IUPAC, 1997
(3, 10)	0.1	$\beta_{(3,10)} = -62.14$	IUPAC, 1997
(4, 2)	0	$\beta^0_{(4,2)} = -1.26$	IUPAC, 1997
(4, 6)	0.1	$\beta_{(4,6)} = -17.60$	IUPAC, 1997
(4, 7)	0	$\beta^0_{(4,7)} = -21.90$	Grenthe, 1992
(5, 3)	0.2	$\beta_{(5,3)} = -16.16$	IUPAC, 1997
Solubility product $\text{UO}_2(\text{OH})_2 \rightleftharpoons \text{UO}_2^{2+} + 2\text{OH}^-$	0	$K^0_{\text{sp}} = -20.87$	Grenthe, 1992

In accordance with the "Law of Mass Action" of Waage and Guldberg (1864), the equilibrium concentrations of the U(VI) hydroxo complex ions $(\text{UO}_2)_m(\text{OH})_n^{2m-n}$, are given from the following equation in molarity units:

$$\left[(\text{UO}_2)_m(\text{OH})_n^{2m-n} \right] = \beta(m, n) \frac{\left[\text{UO}_2^{2+} \right]^m}{\left[\text{H}^+ \right]^n} \quad (2)$$

2.1.2. Carbonato-U(VI) complex ions

When hexavalent uranium is present in an aqueous solution containing carbonate anions, it forms mononuclear and polynuclear carbonato- complexes as well as carbonato- hydroxo- complexes, which are given from the following equations:



while a complex ion is also formed according to Equation 5:



Table 2
Formation constants at 25°C in the presence of carbonates

Species	Ionic strength I (M)	Formation constant values	Reference
$\alpha\text{UO}_2^{2+} + \beta\text{CO}_3^{2-} \rightleftharpoons (\text{UO}_2)_\alpha(\text{CO}_3)_\beta^{2\alpha-2\beta}$			
(1,1)	0	$\beta_{c1}^0 = E+9.68$	Grenthe, 1992
(1,2)	0	$\beta_{c(1,2)}^0 = E+16.94$	Grenthe, 1992
(1,3)	0	$\beta_{c(1,3)}^0 = E+21.60$	Grenthe, 1992
(3,6)	0	$\beta_{c(3,6)}^0 = E+54.00$	Grenthe, 1992
$i\text{UO}_2^{2+} + j\text{CO}_2(\text{aq}) + (k+j)\text{H}_2\text{O}(\text{l}) \rightleftharpoons (\text{UO}_2)_i(\text{CO}_3)_j(\text{OH})_k^{2i-2j-k} + (k+2j)\text{H}^+$			
(2,1,3)	0	$\beta_{c(2,1,3)}^0 = E-17.55$	Grenthe, 1992; Butler, 1998
(11,6,12)	0	$\beta_{c(11,6,12)}^0 = E-63.74$	Grenthe, 1992; Butler, 1998
$3\text{UO}_2^{2+} + \text{CO}_2(\text{aq}) + 4\text{H}_2\text{O}(\text{l}) \rightleftharpoons (\text{UO}_2)_3\text{O}(\text{OH})_2\text{HCO}_3^+ + 5\text{H}^+$	0	$\beta_{c(\text{oxy})}^0 = E-16.04$	Grenthe, 1992; Butler, 1998
Solubility product			
$\text{UO}_2\text{CO}_3 \rightleftharpoons \text{UO}_2^{2+} + \text{CO}_3^{2-}$	0	$K^{\text{osp}c} = E-14.47$	Grenthe, 1992

Ionic strength corrections, at values below 0.31M, for the reactions (4) that are shown in Table 2 and contain dissolved CO₂ molecules in addition to the ionic species, were performed using the following equation:

$$\log \beta = \log \beta^0 + A\Delta z^2 \left(\frac{\sqrt{I}}{\sqrt{I+1}} - 0.31I \right) + 0.11I \quad (6)$$

The last term of the equation (6) takes into consideration the activity coefficient of the dissolved CO₂ neutral species, which usually depends on ionic strength (Ellis *et al.*, 1963; Butler *et al.*, 1998) according to equation (7):

$$\log \gamma_{\text{CO}_2} = 0.11I \quad (7)$$

The equilibrium concentrations in molarity units of the U(VI) carbonato- complex ions and U(VI) carbonato- hydroxo- complex ions are given from the following equations:

$$\left[(\text{UO}_2)_\alpha(\text{CO}_3)_\beta^{2\alpha-2\beta} \right] = \beta_c(\alpha, \beta) \left[\text{UO}_2^{2+} \right]^\alpha \left[\text{CO}_3^{2-} \right]^\beta \quad (8)$$

$$\left[(\text{UO}_2)_i(\text{CO}_3)_j(\text{OH})_k^{2i-2j-k} \right] = \beta_c(i, j, k) \frac{\left[\text{UO}_2^{2+} \right]^i}{\left[\text{H}^+ \right]^{k+2j}} \left[\text{CO}_2 \right]^j \quad (9)$$

$$\left[(\text{UO}_2)_3\text{O}(\text{OH})_2\text{HCO}_3^+ \right] = \beta_c(\text{oxy}) \frac{\left[\text{UO}_2^{2+} \right]^3}{\left[\text{H}^+ \right]^5} \left[\text{CO}_2 \right] \quad (10)$$

2.1.3. Dissolution of atmospheric CO₂

When the only source of carbonates in the aqueous solution is the atmospheric carbon dioxide, the amount of dissolved carbonates is controlled by the following chemical equilibria:



The equilibrium constant K_H , which is known as the Henry's constant, for the reaction (11) at zero ionic strength is shown in Table 3.

Table 3
Henry's constant, K_H , at 25°C

Ionic Strength, I (M)	K_H value	Reference
0	$K_H = E-1.46$	Butler, 1998

Ionic strength corrections at values below 0.31M were performed using the following equation (12), taking into consideration the activity coefficient of the dissolved CO₂ molecules (equation 7):

$$\log K_H = \log K_H^\circ - 0.1 I \quad (12)$$

The aqueous concentration of dissolved CO₂ when the solution is at equilibrium with the atmospheric carbon dioxide is given from equation (13).

$$[CO_2] = K_H \cdot P_{CO_2} \quad (13)$$

The term P_{CO₂} in equation (13) corresponds to the partial pressure of carbon dioxide in the atmosphere (P_{CO₂}=10^{-3.5}atm at 25°C).

2.1.4. Ionization of dissolved CO₂

Carbon dioxide, CO₂, is a diprotic acid and therefore is ionized to produce bicarbonate and carbonate anions, according to the following equations:



The values of the equilibrium constants Ka₁ and Ka₂ of reactions (14) and (15) are given in Table 4. Ionic strength corrections for the reactions (14) and (15) at values below 0.31M were performed using the equations (6) and (1), respectively.

Table 4
 Ionization constants of CO₂ at 25°C

Reactions	Ionic strength, I (M)	Ionization constant values	Reference
CO ₂ + H ₂ O \rightleftharpoons HCO ₃ ⁻ + H ⁺	0	Ka ₁ =E-6.36	Butler, 1998
HCO ₃ ⁻ \rightleftharpoons CO ₃ ²⁻ + H ⁺	0	Ka ₂ =E-10.33	Butler, 1998

The equilibrium concentrations of bicarbonate and carbonate anions can be calculated from the following equations:

$$[HCO_3^-] = Ka_1 \frac{[CO_2]}{[H^+]} \quad (16)$$

$$[CO_3^{2-}] = Ka_2 \frac{[HCO_3^-]}{[H^+]} \quad (17)$$

2.2. Mass balance calculations

2.2.1. The binary UO₂²⁺/H₂O system

The equilibrium molar total concentration of uranium (U_{TOTAL}) in the solution can be expressed as the sum of the equilibrium concentration of all the uranium species that are listed in Table 1.

$$U_{TOTAL} = [UO_2^{2+}] + \sum_{m,n} m [(UO_2)_m (OH)_n]^{2m-n} \quad (18)$$

The mathematical system of equations (2) and (18) consists of sixteen independent equations and eighteen unknowns. Therefore the values of the remaining two unknowns that consist of the solution pH and the equilibrium total concentration of uranium (U_{TOTAL}), have to be set in order to obtain a mathematical solution. The above system of equations is difficult to be solved analytically because it is too complicated. For this reason the MathCad 8.0 software was used, setting the values of pH and U_{TOTAL} and examining whether the UO₂(OH)₂ precipitates or not. The solution of the mathematical system always involves one real positive root for each set of realistic positive values of pH and U_{TOTAL}. Although negative and imaginary roots are also calculated, they are not accepted since they do not have any meaning in nature.

The preceding mathematical system was solved for various ionic strengths (0.01, 0.1, 0.31M) by setting the values of pH and U_{TOTAL} ranging from 2-13 and 10⁻⁵-10⁻²M, respectively.

2.2.2. The ternary UO₂²⁺/CO₃²⁻/H₂O system

In this case the molar total equilibrium concentration of uranium (U_{TOTAL}) can be expressed as the sum of the concentration of all the hydroxo- and carbonato- uranium(VI) complex ions existing in the solution. These species are listed in Tables 1 and 2, respectively.

$$U_{TOTAL} = [UO_2^{2+}] + \sum_{m,n} m [(UO_2)_m (OH)_n]^{2m-n} + \sum_{\alpha,\beta} \alpha [(UO_2)_\alpha (CO_3)_\beta]^{2\alpha-2\beta} + \sum_{i,j,k} i [(UO_2)_i (CO_3)_j (OH)_k]^{2i-2j-k} + 3 [(UO_2)_3 O (OH)_2 HCO_3^+] \quad (19)$$

In such a system the total equilibrium concentration of carbonates C_{TOTAL} can be written as:

$$C_{TOTAL} = [CO_3^{2-}] + [HCO_3^-] + [CO_2] + \sum_{\alpha,\beta} \beta [(UO_2)_\alpha (CO_3)_\beta]^{2\alpha-2\beta} + \sum_{i,j,k} j [(UO_2)_i (CO_3)_j (OH)_k]^{2i-2j-k} + [(UO_2)_3O(OH)_2HCO_3^+] \quad (20)$$

2.2.2.1. Case 1: System at equilibrium with atmospheric carbon dioxide

In an aqueous system at equilibrium with atmospheric carbon dioxide, the concentration of dissolved CO_2 at any ionic strength below 0.31M, is always known as long as it is calculated from the equation (13) (Henry's law). Consequently, the unknown parameters of the mathematical system of the 26 independent equations (2), (8), (9), (10) and (16)-(17) are 28 and thus, the values of two unknowns, that are the solution pH and the equilibrium total concentration of uranium (U_{TOTAL}), have to be set in order to obtain a mathematical solution. However, the system is still complicated and can be solved using the MathCad 8.0 software examining whether the $UO_2(OH)_2$ and UO_2CO_3 precipitate or not.

The mathematical system was solved for various ionic strengths (0.01, 0.1, 0.31M) by setting the values of pH and U_{TOTAL} ranging from 2 - 10 and 1.00E-5 to 1.00E-2M, respectively.

2.2.2.2. Case 2: Closed system at constant C_{TOTAL}

In closed systems, as in the case of underground water, atmospheric carbon dioxide is not at equilibrium with the solution and thus, the dissolved CO_2 can not be calculated from equation (13). In this case, the mathematical system of the 26 independent equations (2), (8), (9), (10) and (16)-(17) has 29 unknown parameters and therefore the values of three parameters have to be set. In addition to the normal setting parameters (U_{TOTAL} and pH), the value of the total concentration of dissolved carbonates C_{TOTAL} was held constant. The mathematical system was solved using the MathCad 8.0 software program for various ionic strengths (0.01, 0.1, 0.31M). The values of C_{TOTAL} and U_{TOTAL} varied from 5.00E-3 to 1.00E-2M and 1.00E-5 to 1.00E-2M respectively, while the value of pH ranged from 2-13.

During the calculations performed, it was found that rutherfordine, UO_2CO_3 , precipitates in the pH region between 4 and 6. In this pH region, the mathematical system was solved with the constraint that the equilibrium uranyl ion concentration ($[UO_2^{2+}]$) is determined from the solubility product of rutherfordine (K_{sp}^c).

3. RESULTS AND DISCUSSION

3.1. The binary UO_2^{2+}/H_2O system

The results, obtained from the solution of the mathematical system of equations that describes chemically the binary UO_2^{2+}/H_2O system, are presented in the form of speciation diagrams illustrated in Figures 1-3. In each diagram, the percent species quotients, $\{(m[(UO_2)_m(OH)_n^{+2m-n}]/U_{TOTAL}) \cdot 100\}$, are plotted as a function of the solution pH for various values of U_{TOTAL} and solution ionic strengths. Due to the large number of uranium(VI) bearing species existing in the binary UO_2^{2+}/H_2O system, only species with a percent quotient greater than 5% are presented in the corresponding figures.

The uranium(VI) speciation diagrams at the lowest studied ionic strength ($I=0.01M$) are presented in Figure 1. As it is shown in Figure 1, the speciation diagrams can be divided in the following four distinct regions.

3.1.1 Region I (pH<3)

In this region, uranyl cations UO_2^{2+} are the only existing uranium(VI) bearing species in the solution. As the total concentration of uranium(VI), U_{TOTAL} , increases, the pH region where the uranyl ion prevails is shrunk. This is not very apparent from Figure 1, but from Figures 2 and 3 in which the speciation diagrams at higher ionic strengths ($I=0.1M$ and $0.31M$ respectively) are presented. Indeed, in a solution with 0.1M ionic strength, $10^{-2}M$ total uranium(VI) concentration and pH=3, only a fraction of about 35% of the hexavalent uranium is present in the form of the uranyl cation. This fraction decreases further to a value of 25% under higher ionic strength ($I=0.31M$) and same U_{TOTAL} in the solution.

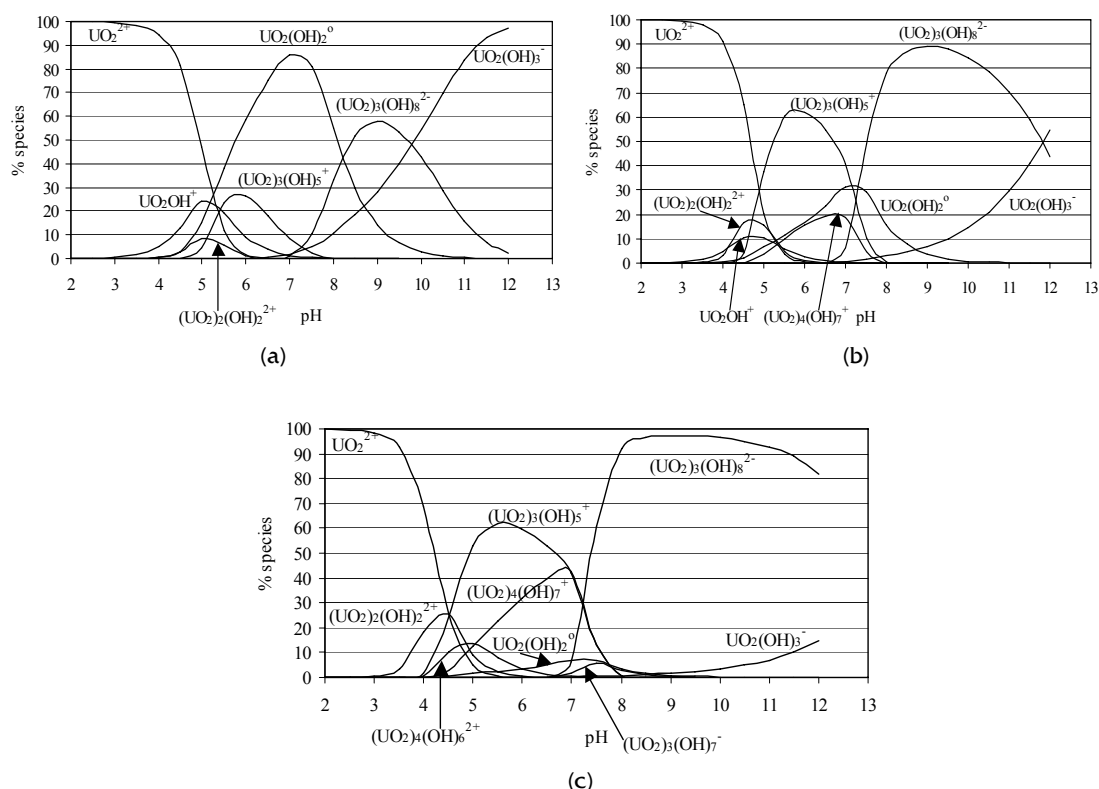


Figure 1. Uranium (VI) speciation diagrams at ionic strength=0.01M and $[U_{TOTAL}]$ equal to (a) E-5M, (b) E-4M and (c) E-3M. In all cases the system is free of carbonates

3.1.2 Region II ($3 < \text{pH} < 6$)

In this region the gradual transformation of the simple uranyl cation to mononuclear and polynuclear hydroxo-uranyl complex ions takes place. The mononuclear complex ions occurring in this region are the positively charged UO_2OH^+ and the neutral species $UO_2(OH)_2^0$. At any ionic strength and low U_{TOTAL} ($10^{-5}M$), the mononuclear species prevail in the solution. As the U_{TOTAL} increases from $1.00E-5M$ to $1.00E-2M$ at any ionic strength (Figures 1-3), the polynuclear complex cations become more and more important in the system and at the greatest studied value of U_{TOTAL} $1.00E-2M$, these species are practically the only existing uranium(VI) bearing species in the solution. The most important polynuclear hydroxo-uranyl complex cations in the region II are: $(UO_2)_3(OH)_5^+$, $(UO_2)_2(OH)_2^{2+}$, $(UO_2)_4(OH)_7^+$, $(UO_2)_4(OH)_6^{2+}$, $(UO_2)_4(OH)_2^{6+}$. The polynuclear complex cation $(UO_2)_3(OH)_5^+$ prevails in the pH region 5-6 under moderate U_{TOTAL} values (10^{-4} - $10^{-3}M$) at any studied value of ionic strength. The cations $(UO_2)_4(OH)_7^+$ and $(UO_2)_4(OH)_6^{2+}$ become more important for the system at pH 6.5-7 and 5 respectively under the higher U_{TOTAL} values ($1.0E-3$ to $1.00E-2M$) and any ionic strength. The cation $(UO_2)_4(OH)_6^{2+}$ prevails in the pH region 2.5-4.5 under extremely high U_{TOTAL} values and ionic strengths (Figures 2-3). Finally, the cation $(UO_2)_2(OH)_2^{2+}$ is important in the pH region 4.5-5 under moderate U_{TOTAL} values ($1.00E-4$ to $1.00E-3M$) at any ionic strength.

The lower and upper pH boundaries of the region II are almost independent of the ionic strength but are strongly dependent on the total concentration of uranium(VI), U_{TOTAL} , in the solution. As the U_{TOTAL} increases, both boundaries shift to lower pH values with the lowest pH boundary responding more to this shift due to the formation of the stable polynuclear complex cation $(UO_2)_4(OH)_2^{6+}$, as it was stated previously.

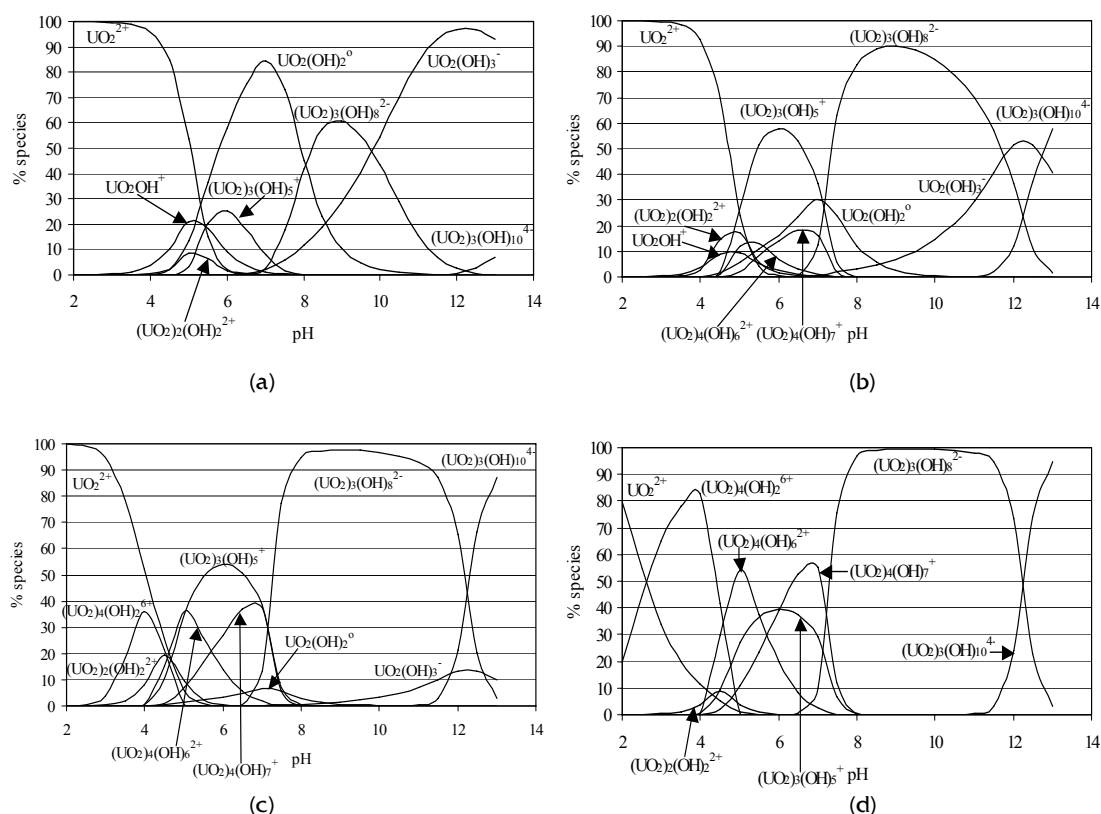


Figure 2. Uranium (VI) speciation diagrams at ionic strength=0.1M and $[U_{TOTAL}]$ equal to (a) E-5M, (b) E-4M, (c) E-3M and E-2M. In all cases the system is free of carbonates

3.1.3. Region III ($6 < \text{pH} < 8$)

In this region, a chemical change from positively charged species to negatively charged species takes place. The neutral aqueous species $UO_2(OH)_2^0$ prevails in this region under very low U_{TOTAL} values at any ionic strength (Figures 1-3). This neutral species becomes less important for the system as the total uranium(VI) concentration increases in the solution. Two anions are formed in this region, the polynuclear complex $(UO_2)_3(OH)_8^{2-}$ and the mononuclear complex $UO_2(OH)_3^-$. In all cases, the polynuclear complex anion is found at higher concentration in the solution than the mononuclear complex anion. The concentration of the latter diminishes substantially as the solution becomes more concentrated in hexavalent uranium while remaining independent of the ionic strength under the same U_{TOTAL} values in the solution. Finally, both pH boundaries of this region shift to lower pH values as both the total concentration of uranium(VI), U_{TOTAL} , and the ionic strength of the solution increases. For example, region III shifts to the pH region 5-7 when the U_{TOTAL} is equal to 1.00E-2M and the ionic strength is 0.31M.

3.1.4. Region IV ($\text{pH} > 8$)

In this region, the negatively charged species $(UO_2)_3(OH)_8^{2-}$, $(UO_2)_3(OH)_{10}^{4-}$ and $UO_2(OH)_3^-$ prevail in the solution. Practically, the solution is composed only of these three uranium bearing complex anions at high total uranium(VI) concentration. At low U_{TOTAL} values, the neutral aqueous species $UO_2(OH)_2^0$ is present in the solution but its concentration diminishes steeply with increasing pH. The polynuclear complexes $(UO_2)_3(OH)_8^{2-}$ and $(UO_2)_3(OH)_{10}^{4-}$ are more important than the mononuclear $UO_2(OH)_3^-$ anion under higher U_{TOTAL} and ionic strength values. The $(UO_2)_3(OH)_8^{2-}$ anion prevails in moderate alkaline solutions with a concentration peak in the pH region 8-10. As the U_{TOTAL} and the ionic strength of the solution increase, the region where the $(UO_2)_3(OH)_8^{2-}$ anion prevails is expanded so that under the highest studied U_{TOTAL} 1.00E-2M and ionic strength 0.31M, this anion is the only uranium(VI) bearing species in the solution at pH values between 7.5 and 11.5. The other polynuclear complex anion, $(UO_2)_3(OH)_{10}^{4-}$, prevails in highly alkaline solutions at pH values higher than 12 under high U_{TOTAL} and ionic strength values. The $UO_2(OH)_3^-$ anions are

important at low total uranium(VI) concentrations having a concentration peak at pH 12. They prevail in solution under the lowest studied U_{TOTAL} , $10^{-5}M$, and at pH values higher than 10. At higher U_{TOTAL} values, they gradually lose their significance in the system.

Finally, the pH boundary of this region depends on the total uranium(VI) concentration and the ionic strength of the solution. In general, the pH boundary shifts to lower pH values as both the U_{TOTAL} and the ionic strength increase. Indeed, the pH boundary, above which the negatively charged uranium(VI) species predominate, shifts to the pH value of 6.7 under the highest studied U_{TOTAL} ($1.00E-2M$) and ionic strength ($0.31M$) values.

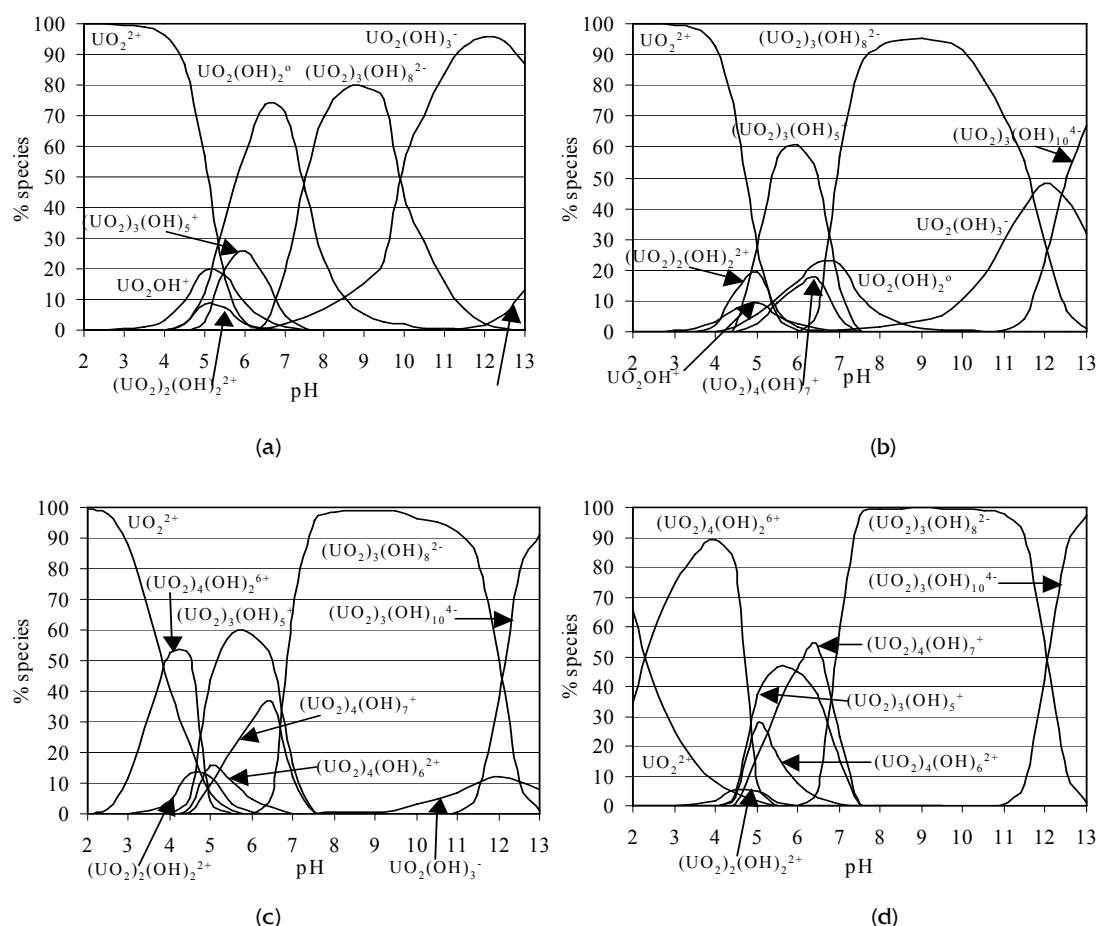


Figure 3. Uranium (VI) speciation diagrams at ionic strength=0.31M and $[U_{TOTAL}]$ equal to (a) E-5M, (b) E-4M, (c) E-3M and E-2M. In all cases the system is free of carbonates

3.2. The ternary $UO_2^{2+}/CO_3^{2-}/H_2O$ system

The effect of the presence of carbonates on hexavalent uranium speciation in aqueous solutions has been studied in open and closed systems. An open system simulates an aqueous solution in contact with air that contains carbon dioxide and is proper for the description of chemical phenomena occurring in surface and ground water. A closed system simulates an aqueous solution that is not in contact with air. In such a system, the content of carbonates in the aqueous phase is not controlled by the dissolution of the atmospheric carbon dioxide but by the prevailing geochemical conditions (e.g. dissolution of carbonaceous materials). Therefore, a closed system is proper for the description of chemical phenomena occurring mainly in underground water.

3.2.1. The ternary $\text{UO}_2^{2+}/\text{CO}_3^{2-}/\text{H}_2\text{O}$ open system

The U(VI) speciation diagrams in an aqueous solution at equilibrium with the atmospheric carbon dioxide are presented in Figures 4, 5 and 6 for several values of U_{TOTAL} and solution ionic strength.

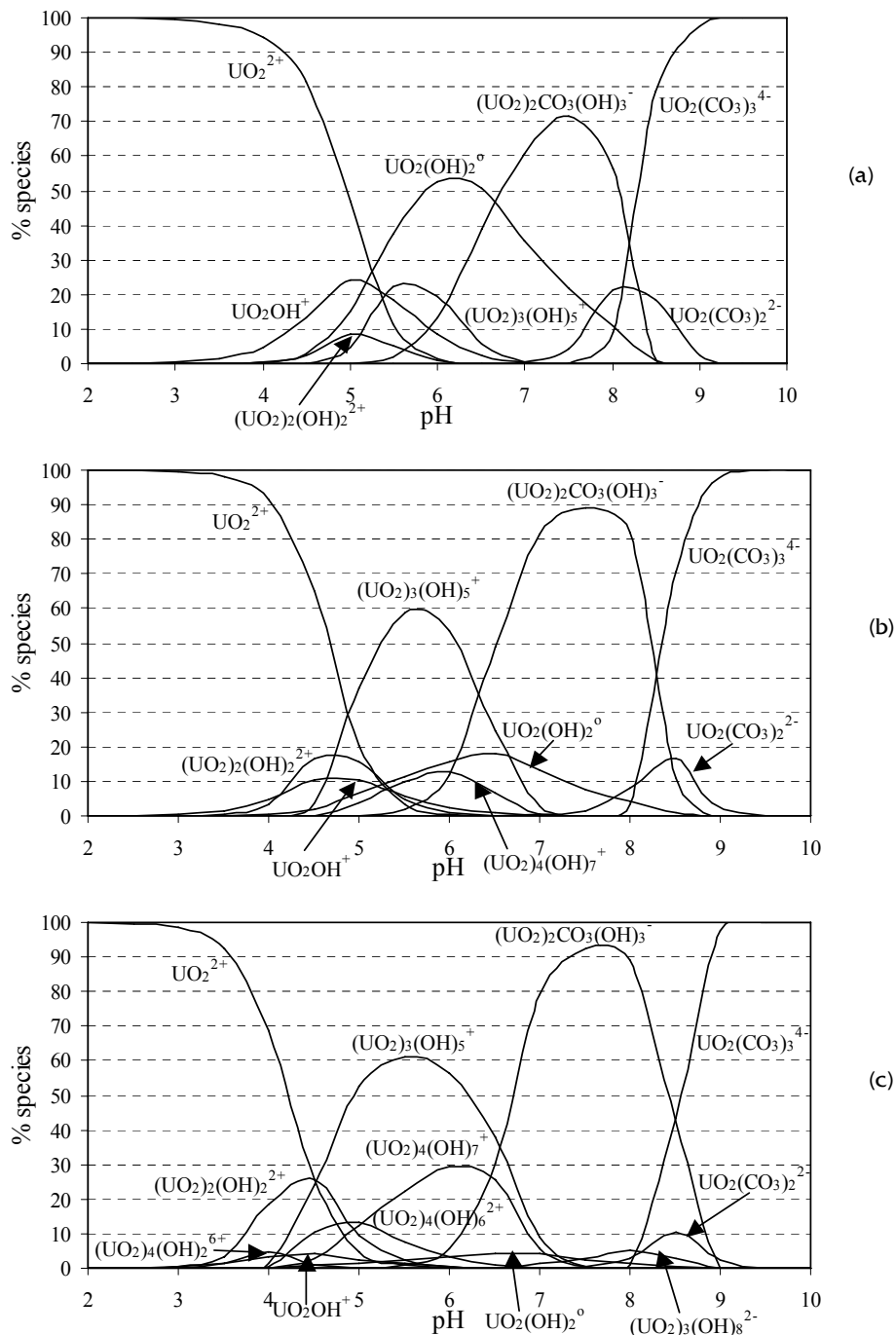


Figure 4. Uranium (VI) speciation diagrams at ionic strength=0.01M and $[\text{U}_{\text{TOTAL}}]$ equal to (a) E-5M, (b) E-4M and (c) E-3M. In all cases the system is open

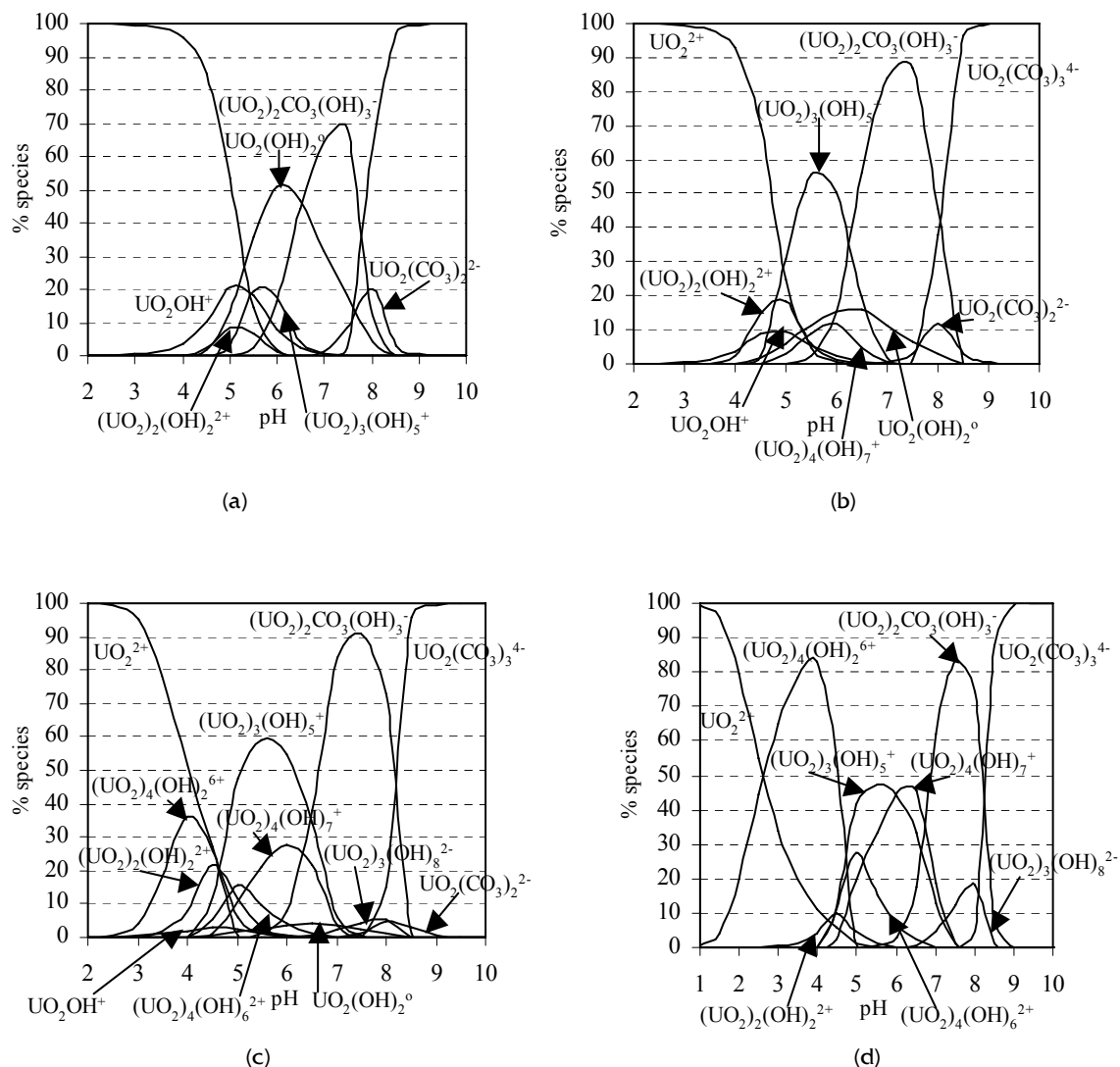


Figure 5. Uranium (VI) speciation diagrams at ionic strength=0.1M and $[U_{TOTAL}]$ equal to (a) E-5M, (b) E-4M, (c) E-3M and (d) E-2M. In all cases the system is open

The following three distinct pH regions can be observed.

3.2.1.1. Region I (pH<3)

This region is exactly identical with the region I that has been previously described in the binary UO_2^{2+}/H_2O system. U(VI) exists exclusively in the solution with the form of uncomplexed uranyl cations UO_2^{2+} although the dissolved total carbonates concentration of the aqueous phase, C_{TOTAL} , is $1.00E-5M$. This is attributed to the fact that under high acidic conditions (pH<3), the 100% of the dissolved total carbonates are present in the solution in the form of undissociated $CO_2(aq)$ species having negligible complexing ability as shown in the speciation diagrams of dissolved carbonates presented in Figure 7. Therefore, the conclusions that were drawn for the region I of the binary UO_2^{2+}/H_2O system, are still valid for the same pH region of the ternary $UO_2^{2+}/CO_3^{2-}/H_2O$ open system.

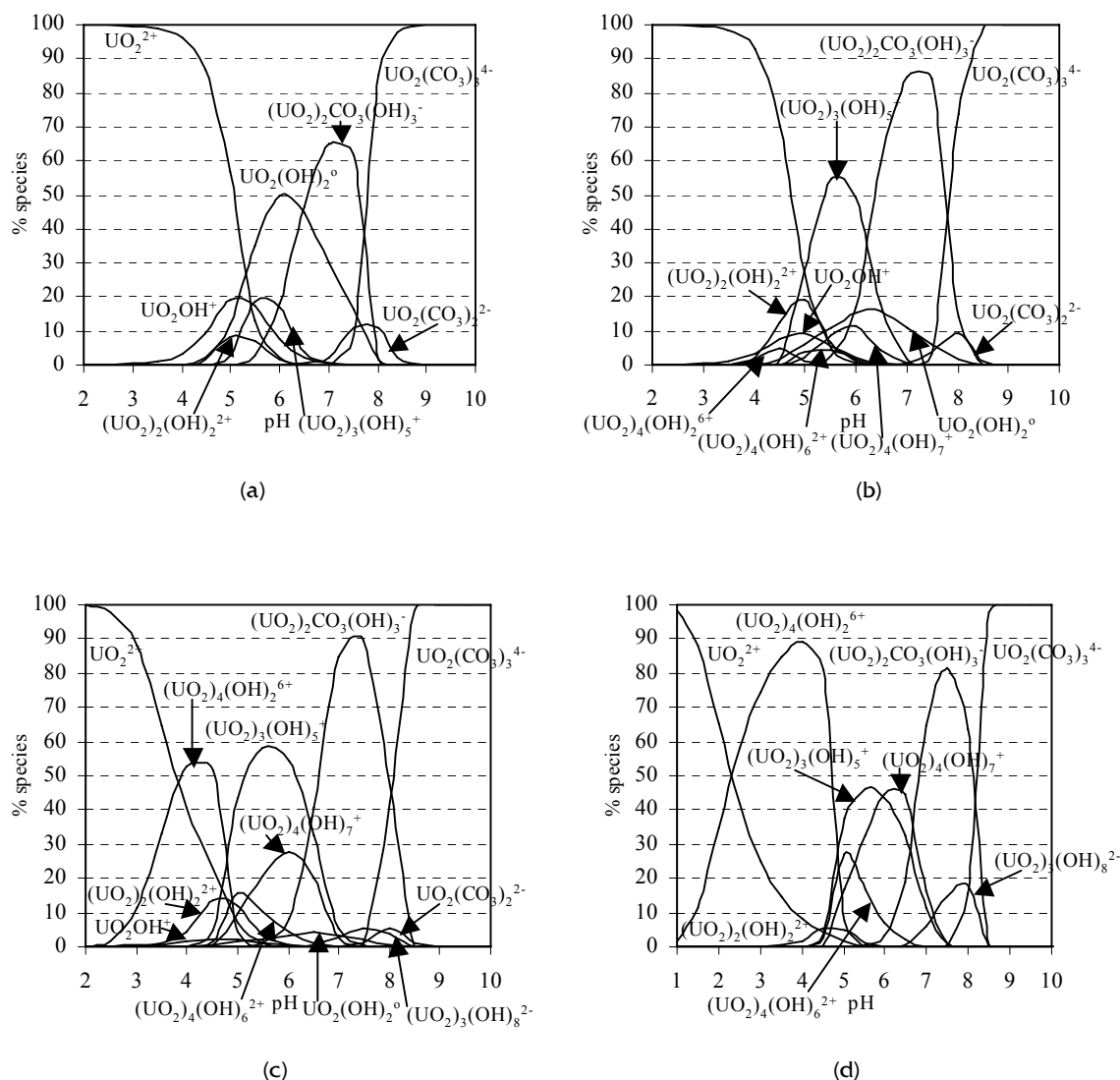


Figure 6. Uranium (VI) speciation diagrams at ionic strength=0.31M and $[U_{TOTAL}]$ equal to (a) E-5M, (b) E-4M, (c) E-3M and (d) E-2M. In all cases the system is open

3.2.1.2. Region II ($3 < pH < 6$)

In this region the uranyl cation is gradually transformed to mononuclear and polynuclear hydroxo complexes. From this point of view, region II has many similarities with the corresponding region II of the binary UO_2^{2+}/H_2O system. Therefore, the conclusions drawn for the region II of the binary UO_2^{2+}/H_2O system are principally the same with the ones drawn for the region II of the ternary $UO_2^{2+}/CO_3^{2-}/H_2O$ open system. The only difference in the region (II) of the binary UO_2^{2+}/H_2O and open ternary $UO_2^{2+}/CO_3^{2-}/H_2O$ systems is the occurrence of the mixed carbonato-hydroxo U(VI) complex ion $(UO_2)_2CO_3(OH)_3^-$. This anion begins to form at $pH=5$ and it never predominates in the system in this pH region, as shown in Figures 4-6. The $(UO_2)_2CO_3(OH)_3^-$ ion plays an important role in the ternary $UO_2^{2+}/CO_3^{2-}/H_2O$ open system because it marks the transformation of the U(VI) aqueous species from the hydroxo complexes to the carbonato complexes.

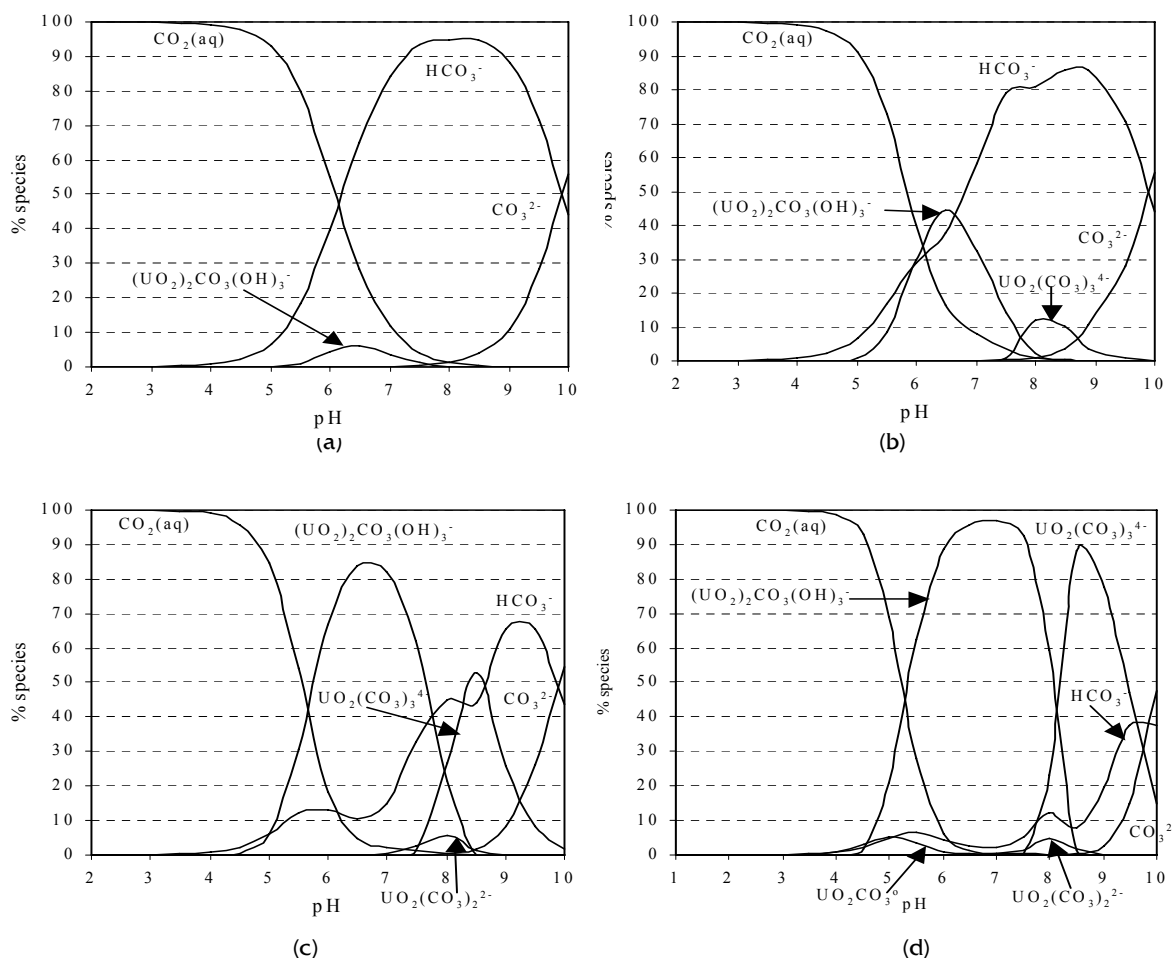


Figure 7. Speciation diagrams of dissolved carbonates at ionic strength=0.1M and $[\text{U}_{\text{TOTAL}}]$ equal to (a) E-5M, (b) E-4M, (c) E-3M and (d) E-2M

3.2.1.3. Region III (pH>6)

In region (III), the hydroxo U(VI) complexes are transformed gradually to carbonato U(VI) complexes. This transformation takes place through the formation of the mixed carbonato-hydroxo U(VI) complex ion $(\text{UO}_2)_2\text{CO}_3(\text{OH})_3^-$. This mixed complex ion reaches a peak in the pH region 7-8, whose absolute value becomes maximum (about 90%) under intermediate U_{TOTAL} values ($1.00\text{E}-4$ to $1.00\text{E}-3\text{M}$) at any studied ionic strength. At lower U_{TOTAL} values (10^{-5}M) and any ionic strength, the mixed complex ion $(\text{UO}_2)_2\text{CO}_3(\text{OH})_3^-$ predominates in the solution but coexists with significant amounts of $\text{UO}_2(\text{OH})_2^0$, $\text{UO}_2(\text{CO}_3)_2^{2-}$ and $\text{UO}_2(\text{CO}_3)_3^{4-}$ complex ions. At the highest studied U_{TOTAL} value of 10^{-2}M and any ionic strength, $(\text{UO}_2)_2\text{CO}_3(\text{OH})_3^-$ complex ion predominates but coexists with significant amounts of $(\text{UO}_2)_3(\text{OH})_5^+$, $(\text{UO}_2)_4(\text{OH})_7^+$, $(\text{UO}_2)_3(\text{OH})_8^{2-}$ and $\text{UO}_2(\text{CO}_3)_3^{4-}$ complex ions in the solution.

For pH higher than 8 and at any ionic strength, all U(VI) complex ions of the solution are transformed to the $\text{UO}_2(\text{CO}_3)_3^{4-}$ complex ion which is the thermodynamic stable chemical uranium species of the ternary $\text{UO}_2^{2+}/\text{CO}_3^{2-}/\text{H}_2\text{O}$ open system. This species is the only occurring U(VI) species in the solution at pH higher than 9. The ternary $\text{UO}_2^{2+}/\text{CO}_3^{2-}/\text{H}_2\text{O}$ open system has been studied up to the pH value of 10 because the dissolved total carbonates concentration of the aqueous phase C_{TOTAL} exceeds the value of 0.3M at higher pH values as shown in Figure 8. Therefore, correction of species activities at high ionic strength ($>0.31\text{M}$) had to be performed, the accuracy of which is questionable. Thus, the ternary $\text{UO}_2^{2+}/\text{CO}_3^{2-}/\text{H}_2\text{O}$ open system was studied in the pH region 1-10 in which the thermodynamic data are accurate. From Figure 8 it is obvious that the dissolved total carbonates concentration of the aqueous phase C_{TOTAL} remains low and constant at pH values lower than 6. At higher pH values (pH>6), the solubility of carbonates increases steeply marking the transformation of hydroxo U(VI) complex ions to carbonato U(VI) complex ions through the mixed complex $(\text{UO}_2)_2\text{CO}_3(\text{OH})_3^-$ ion as it was stated previously.

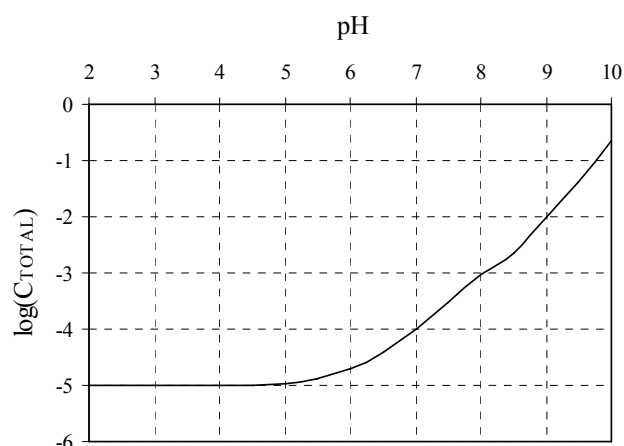


Figure 8. Total dissolved carbonates concentration in molar units as a function of pH (open system, $U_T = 5 \times 10^{-5} M$, ionic strength 0.31M, 25°C)

3.2.2. The ternary $UO_2^{2+}/CO_3^{2-}/H_2O$ closed system

The ternary $UO_2^{2+}/CO_3^{2-}/H_2O$ closed system was studied under conditions of constant total carbonate concentration, C_{TOTAL} , in the solution. The values of C_{TOTAL} used in this study varied in the region 300-600mg/l (5.00×10^{-3} to $1.00 \times 10^{-2} M$) which represents values that commonly occur in underground waters. In relation to the $UO_2^{2+}/CO_3^{2-}/H_2O$ open system, these C_{TOTAL} values are extremely high for the entire acidic region, the neutral region and the mildly alkaline region as it can be observed by simply comparing the carbonate solubility values presented in Figure 8. The speciation diagrams in a solution containing total hexavalent uranium concentration $1.00 \times 10^{-4} M$ under 0.31M ionic strength are given in Figure 9 as a function of C_{TOTAL} . From Figure 9 is clear that the high total carbonate concentration in the solution results in the precipitation of rutherfordine (UO_2CO_3) in the acidic pH region 4.5-5.7. As is shown in Figure 10, the minimum hexavalent uranium solubility is observed at pH approaching 5 and at any instant is higher than $2.00 \times 10^{-5} M$.

In the speciation diagrams shown in Figure 9, the part that corresponds to this pH region has been constructed taking into consideration that the solution is saturated with rutherfordine and thus the uranyl ion and the free carbonates concentrations are dependent variables in this system. The speciation diagrams shown in Figure 9 are divided in the following three distinct regions.

3.2.2.1. Region I (pH<3)

This is a common pH region for both the binary UO_2^{2+}/H_2O and the open and closed ternary $UO_2^{2+}/CO_3^{2-}/H_2O$ systems. In this pH region, there is a scarcity of a strong complexing agent in the solution and thus the hexavalent uranium is present with the form of uranyl cations (UO_2^{2+}).

3.2.2.2. Region II (3<pH<11)

In this pH region, uranyl cations lose their thermodynamic stability and are transformed directly to carbonate U(VI) complexes. This is an important difference in the aqueous U(VI) chemistry between the closed and the open ternary $UO_2^{2+}/CO_3^{2-}/H_2O$ systems. The calculations performed in this work showed that the concentration of the bicarbonate ion (HCO_3^-) in the pH region of the uranyl cation transformation ($3 < pH < 5$) is at least 1000 times lower in the case of an open system than in the case of the studied closed system. This is attributed to the extremely high total carbonate concentrations C_{TOTAL} in the entire acidic region of the studied closed systems in relation to the values of the carbonate solubility under the same conditions in an open system. Due to the lack of sufficient bicarbonate ion concentration in an open system, uranyl cations are transformed firstly to hydroxo U(VI) complexes ($3 < pH < 6$) and later to carbonate U(VI) complexes ($pH > 6$) as is shown in Figures 4-6. On the contrary, due to the high bicarbonate ion concentration in a closed system, there is high potential for the uranyl cation complexation and thus hexavalent uranium begins to form complexes with dissolved carbonates at very low pH values as shown in Figure 9.

The most important complexes, that are formed in this region II, are the following: $UO_2CO_3^0$, $(UO_2)_2CO_3(OH)_3^-$, $UO_2(CO_3)_2^{2-}$ and $UO_2(CO_3)_3^{4-}$. The $UO_2CO_3^0$ complex species has a concentration peak at a pH value very closed to 5 and is the predominant species in the pH region where rutherfordine (UO_2CO_3)

has precipitated (Figure 9), as expected. The increase of the uranium(VI) solubility at pH values higher than 5 (Figure 10) is attributed to the formation of $(\text{UO}_2)_2\text{CO}_3(\text{OH})_3^-$ and $\text{UO}_2(\text{CO}_3)_2^{2-}$ complex ions that exhibit concentration peaks at pH values of 5.5 and 6, respectively. The carbonate U(VI) complex ion that dominates the closed ternary $\text{UO}_2^{2+}/\text{CO}_3^{2-}/\text{H}_2\text{O}$ system is the $\text{UO}_2(\text{CO}_3)_3^{4-}$ anion. This anion prevails in the solution in the pH region 6.5-11.5 and is almost the only aqueous uranium(VI) species in the solution in the pH region 8-11.

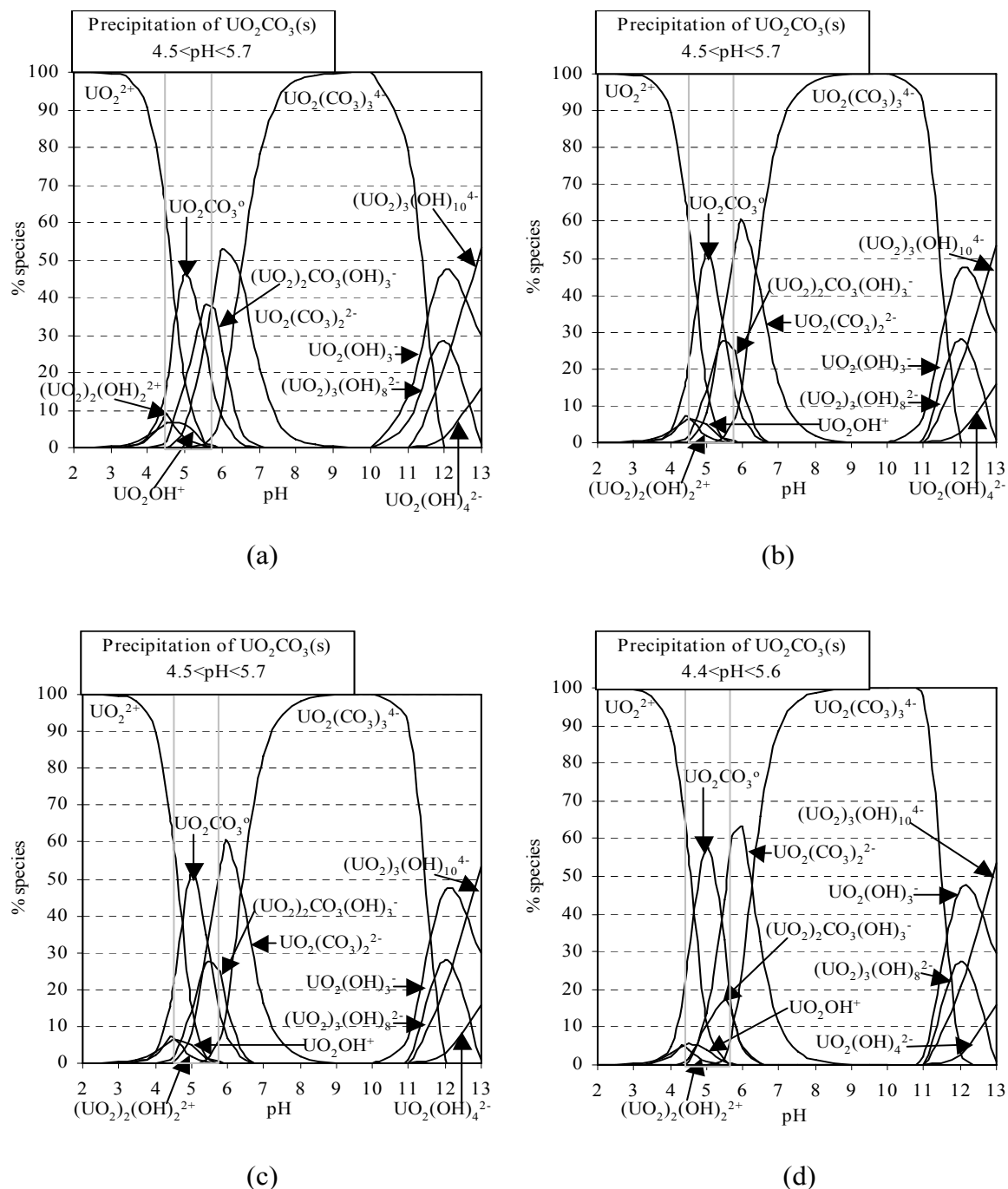


Figure 9. Uranium(VI) speciation diagrams at ionic strength 0.31M, U_{TOTAL} E-4M under constant total carbonate concentration C_{TOTAL} (a) 300mg/l, (b) 400mg/l, (c) 500mg/l and (d) 600mg/l at 25°C.

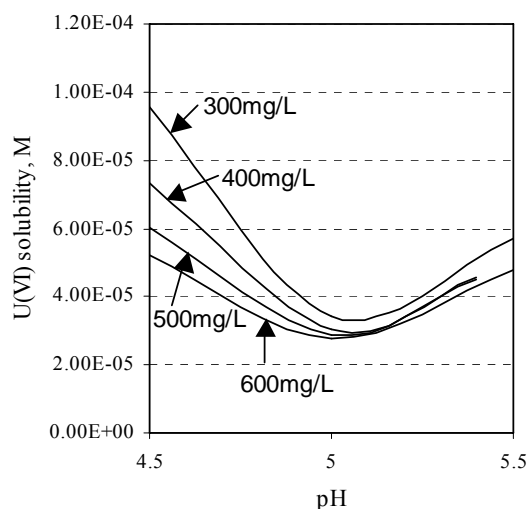


Figure 10. Uranium(VI) solubility as a function of pH and total carbonate concentration in a solution with 0.31M ionic strength

3.2.2.3. Region III (pH>11)

In this pH region, the $\text{UO}_2(\text{CO}_3)_3^{4-}$ anion loses its thermodynamic stability in favor of hydroxo U(VI) complexes. $\text{UO}_2(\text{CO}_3)_3^{4-}$ anion is transformed drastically to the $\text{UO}_2(\text{OH})_3^-$, $(\text{UO}_2)_3(\text{OH})_8^{2-}$, $(\text{UO}_2)_3(\text{OH})_{10}^{4-}$ and $\text{UO}_2(\text{OH})_4^{2-}$ within the pH region 11-12. At pH higher than 12, hexavalent uranium occurs in the solution exclusively in the form of hydroxo U(VI) anions.

4. CONCLUSIONS

The dioxo-uranium speciation calculations provided useful data for the aqueous U(VI) chemistry in the binary $\text{UO}_2^{2+}/\text{H}_2\text{O}$ and the ternary $\text{UO}_2^{2+}/\text{CO}_3^{2-}/\text{H}_2\text{O}$ systems.

The most important feature of the binary $\text{UO}_2^{2+}/\text{H}_2\text{O}$ system is the observed sequential transformation of the free uranyl cation to positively charged hydroxo-U(VI) complex ions and then to negatively charged hydroxo-U(VI) complex ions as pH increases from the acidic to the alkaline region. This alteration in the chemical composition of the aqueous species of hexavalent uranium affects drastically its chemical behaviour and activity (Krestou *et al.*, 2002; Krestou *et al.*, 2003).

The presence of potential ligands such as carbonates substantially changes the chemical composition of uranium(VI) species in the solution. The ternary $\text{UO}_2^{2+}/\text{CO}_3^{2-}/\text{H}_2\text{O}$ system has been studied in both an open system, which simulates an aqueous solution at equilibrium with atmospheric $\text{CO}_2(\text{g})$, and a closed system, which simulates an aqueous solution under various geochemical conditions. The main feature of the ternary $\text{UO}_2^{2+}/\text{CO}_3^{2-}/\text{H}_2\text{O}$ system in relation to the binary $\text{UO}_2^{2+}/\text{H}_2\text{O}$ system is the formation of carbonato-U(VI) complex ions within an extended pH region.

It is very crucial to mention here that in the closed ternary $\text{UO}_2^{2+}/\text{CO}_3^{2-}/\text{H}_2\text{O}$ system a sequential transformation from the uranyl cation through the carbonato U(VI) complex ions to hydroxo U(VI) complex anions takes place as the solution pH increases. On the contrary, in the open ternary $\text{UO}_2^{2+}/\text{CO}_3^{2-}/\text{H}_2\text{O}$ system a sequential transformation from the uranyl cation through the hydroxo U(VI) complex ions to carbonato U(VI) complex anions is observed as the solution pH increases. This is the main difference in the aqueous hexavalent uranium chemistry between the open and the closed ternary $\text{UO}_2^{2+}/\text{CO}_3^{2-}/\text{H}_2\text{O}$ systems attributed to differences in the mass action of the complexing agents OH^- , HCO_3^- and CO_3^{2-} .

In an open or a closed ternary $\text{UO}_2^{2+}/\text{CO}_3^{2-}/\text{H}_2\text{O}$ system and at pH lower than 3, the concentrations (mass actions) of the complexing agents are negligible. Therefore, there is no potential for complexation in the solution and the hexavalent uranium occurs in the form of uranyl cations.

In an open system and in the pH region 3-6, the complexing ability of hydroxide ions is greater than that of the carbonaceous bearing ions although their concentrations in the solution are comparable. This is attributed to the very low solubility of atmospheric carbon dioxide under that conditions (Figure 8) and to the higher formation constants of hydroxo-U(VI) complexes in relation to the formation constants of carbonato-U(VI) complexes (Tables 1-2).

In an open system and at pH values higher than 6, carbonaceous complexing agents prevail against hydroxide ion complexing agent because their concentration in the solution is much higher than that of the hydroxide ion due to the substantial increase of the solubility of atmospheric carbon dioxide under these conditions (Figure 8).

In a closed system and in the pH region 3-11, the concentrations of carbonaceous complexing agents are much higher than the one of the hydroxide ion, due to the high total dissolved carbonates concentration of the system, and thus their complexing ability prevails the corresponding one of the hydroxide ion.

Finally, in a closed system and at pH values higher than 11, the concentration of hydroxide ion is comparable or greater than the one of the free carbonate ion. Therefore, taking into account the higher formation constants of hydroxo-U(VI) complexes in relation to the formation constants of carbonato-U(VI) complexes, it can be concluded that the OH⁻ complexing agent prevails against the CO₃²⁻ complexing agent.

REFERENCES

- Butler, J.N. and Cogley, D.R., *Ionic equilibrium: Solubility and pH calculations*. Willey Interscience, 1998, 367-372.
- Combkoto, I., Kovacs, F., Bohm, J., Debreczeni, A., Removal of uranium from contaminated groundwater at a former uranium mining site. Proceedings of the 1st IMAGE-TRAIN Cluster Meeting November 7-8, 2001, pp. 97-102, Karlsruhe, Germany.
- Ellis, A.J. and Golding, R.M., The solubility of carbon dioxide above 100°C in water and in sodium chloride solutions. *American Journal of Science*, 1963, 261, 47-60.
- Gabriel, U., Gaudet, J.-P., Spadini, L., Charlet, L., Reactive transport of uranyl in geothite column: an experimental and modelling study. *Chemical Geology*, 1998, 115, 107-128.
- Grenthe, I., Fuger, J., Konings, R. J. M., Lemire, R. J., Muller, A. B., Cregu, C. N-T., Wanner, H., *Chemical thermodynamics Vol 1: Chemical thermodynamics of uranium*, Nuclear Energy Agency, North-Holland, 1992, 86, 306 p.
- IUPAC (International Union of Pure and Applied Chemistry), (The) Stability Constants Database, Version 3.10, by L. Pettit and K. Powel, Copyright 1997, Academic Software and IUPAC Commission on Equilibrium Data.
- Krestou, A., Panias, D., Xenidis, A., Paspaliaris, I., Uranium Removal from Aqueous Solutions using Natural Zeolite. Proceedings of the 7th International Symposium on Environmental Issues and Waste Management in Energy and Mineral Production (SWEMP 2002), 07-10 October 2002, pp. 795-802, Cagliari, Sardinia, Italy.
- Krestou, A., Xenidis, A., Panias, D., Mechanism of aqueous uranium(VI) uptake by natural zeolitic tuff. *Minerals Engineering*, 2003, 16, 1363-1370.
- Lee, J.D., *Concise Inorganic Chemistry*. 4th edition, 1991, Chapman&Hall, 890-895.
- PEREBAR, Long-term Performance of Permeable Reactive Barriers used for the Remediation of Contaminated groundwater, 1999, <http://www.pereber.bam.de>.
- Rostker, B., Environmental Exposure Report. Department of Defense, 1998 <http://www.gulflink.osd.mil/du/index.html>
- Veselic, M., Gantar, I., Karahodzic, M., Galicic, B., Towards Passive Treatment of Uranium Mine Waters. Proceedings of the 1st IMAGE-TRAIN Cluster Meeting, November 7-8, 2001, pp. 116-128, Karlsruhe, Germany.
- Waage, P. and Guldberg, C.M., *Forhandlinger: Videnskabs-Selskabet i Christiania*. 1864, 35.
- Zajic, V.S., Review of Radioactivity, Military Use, and Health Effects of Depleted Uranium. 1999, <http://members.tripod.com/vzajic>.
- Zamora, M.L., Tracy, B.L., Zielinski, J.M., Meyerhof, P.D, Moss, M.A, Chronic Ingestion of Uranium in Drinking Water: A study of kidney bio-effects in humans. *Toxicological Sciences*, 1998, 43, 68-77.