Section 4. Spent fuel disposal studies

# Modeling the solubility of zirconia in a repository for high-level radioactive waste

E. Curti *, W. Hummel

*Waste Management Laboratory, Paul Scherrer Institute, CH-5232 Villigen PSI, Switzerland*

## Abstract

The solubility of zirconia in a typical radioactive waste repository environment is examined in the light of available thermodynamic data, with particular focus on the influence of carbonate complexes. Using tetravalent actinides as chemical analogues, values for the stability constants of two Zr–carbonate complexes have been estimated. The solubility of monoclinic zirconia in a typical repository pore water has been then calculated with the help of a speciation model. Although our calculations indicate that the solubility of zirconia in a bentonite-filled repository environment will probably be between $10^{-9}$ and $10^{-8}$ M, there are large unavoidable uncertainties in these predictions, due to limitations in the available thermodynamic data. Similarly, although leaching experiments suggest that dissolution rates of zirconia are much smaller than for borosilicate glass, this comparison is inconclusive in view of the short leaching times involved in tests performed with zirconia. There is therefore a need for further solubility and kinetic studies of zirconia to assess the stability of this material in a radioactive waste disposal environment. © 1999 Elsevier Science B.V. All rights reserved.

## 1. Introduction

Recently, there has been a renewed interest in inert matrix fuels (IMF), as a means to reduce the increasing stockpile of fissile Pu arising from operation of light water reactors [1]. These fuels would be more efficient than mixed oxide fuels (MOX) in burning the accumulating Pu stockpile, since they are U-free and hence do not generate Pu through neutron activation. The use of IMF is also prompted by the politically induced abandonment of fast reactor systems, which use Pu instead of U as a fissile material.

One of the materials proposed as inert matrix for Pu fuel is cubic zirconia (c-$ZrO_2$). Although metastable at reactor operation temperatures (the thermodynamically stable phase being monoclinic), a cubic phase is desirable because of its capability to form isomorphous solid solutions with the fuel component $PuO_2$ [1]. In order to obtain fully stabilised solid solutions with cubic symmetry, it is necessary to mix the Zr oxide with other

divalent or trivalent metal oxides (typically rare earth oxides), so that the resulting fuel pellets will contain about 10 at.% $PuO_2$ and 15% yttria or lanthanide oxides [2]. The pellets would then be assembled in rods protected by zircalloy cladding as in U-fuelled light water reactors.

In this paper, we focus on the long-term durability of $ZrO_2$-spent fuel when it is disposed, without reprocessing, in a typical repository for high-level radioactive waste [3]. The aim is to evaluate whether the conditions prevailing in such a repository are capable of enhancing the solubility of zirconia, which is thought to be very low in pure water [4]. To this purpose, critical thermodynamic data on Zr-complex formation have been reviewed, and the effect of dissolved ligands present in the pore water permeating a typical repository environment has been evaluated.

## 2. Scenario for IMF-waste degradation in the repository

A repository concept similar to that developed in Switzerland for vitrified or spent high-level waste is assumed [3]. Following this concept, the spent IMF would

---

* Corresponding author. Tel.: +41-56 310 2416; fax: +41-56 310 2821; e-mail: enzo.curti@psi.ch

be disposed at a depth of about 1 km in tunnels excavated within a suitable host rock and finally sealed with compacted bentonite.

Once the ground water has accessed the waste, degradation reactions would start and release of the radionuclides would take place. After coming in contact with an aqueous phase at low temperature (313–333 K), cubic zirconia should be transformed into its monoclinic modification (m-$ZrO_2$), which is the stable phase at low temperature. Thus, in this exercise it is assumed that a thin surface film of monoclinic zirconia forms on the surface of the waste matrix. This film determines the solubility of the waste material.

The release of dissolved radionuclides from a repository depends on many transport and chemical parameters (see e.g. ch. 5.2 in Ref. [3]). For radionuclides with high solubility limits, like $^{135}$Cs and $^{59}$Ni, the solubility and kinetic behavior of the waste matrix are important controlling factors. For instance, an insoluble and slowly corroding matrix will contribute to reduce the diffusive fluxes of such radionuclides into the geosphere. In this paper, we will focus on the comparison of matrix solubilities. Particularly, the solubility of zirconia in the repository environment will be compared with that of conventional vitrified waste and $(U,Pu)O_2$ spent fuel.

## 3. The solubility of monoclinic zirconia

### 3.1. Previous work

The solubility of m-$ZrO_2$ has been studied experimentally and theoretically by Adair et al. [4] over a wide temperature range (298–573 K). Unfortunately, experimental determinations were limited either to very low or very high pH (lower than 4 or larger than 11), thus not covering the milder conditions prevailing in most geologic environments, including a high-level waste repository. In both acid and alkaline solutions high Zr equilibrium concentrations, ranging between $10^{-6}$ and $10^{-3}$ M, were determined.

The solubility of monoclinic zirconia in the intermediate pH-region was merely extrapolated through speciation calculations based on available thermodynamic data. Basically, the constants used by Adair et al. [4] are those published and recommended in the review of Baes and Mesmer [5]. According to these data, above pH 6 the complex $Zr(OH)_5^-$ dominates over all other hydroxide species.

Adairs' calculations predict a very low solubility ($10^{-11}$–$10^{-9}$ M) for m-$ZrO_2$ in the pH region of interest for waste disposal (pH $\sim$ 7–9). Such low solubilities would mean that zirconia is practically an inert waste matrix. Unfortunately, the lack of a direct experimental confirmation casts some doubts on the validity of these

concentration limits, especially considering that these have been extrapolated from the results of investigations carried out far outside the pH region of interest, where the solubility of zirconia is quite high [5].

The picture is further complicated by the incoherence of the data found in the literature. In a recent review of Zr thermodynamic data by Aja et al. [6], the importance of the pentahydroxide complex is contested. According to these authors, the predominating hydroxide species is $Zr(OH)_4^0$, which results in a very high solubility of baddeleyite (natural m-$ZrO_2$) in the near-neutral pH region (about $10^{-3}$ M at 298 K, see Fig. 7 in Ref. [6]). This high solubility, which is many orders of magnitude above the value calculated by Adair et al. [4], follows from the large value selected by Aja et al. [6] for the cumulative formation constant of $Zr(OH)_4^0$ ($\log \beta_{4,OH}^0$ = 54.4 vs. 46.3 as extracted from Baes and Mesmer's compilation). Such Zr concentrations appear to be unreasonably high knowing that m-$ZrO_2$ is considered to be an insoluble compound by experienced laboratory chemists (see e.g. Ref. [7]).

### 3.2. Complex formation with carbonate and other ligands

Aja et al. [6] reviewed the complexation of Zr with various anionic ligands ($F^-$, $SO_4^{2-}$, $NO_3^-$, and $Cl^-$). Due to the low to moderate concentrations of these ligands in the ground water percolating through the Swiss crystalline basement (Table 2), such complexes will certainly be insignificant in such a repository environment.

Neither Aja et al. [6] nor Adair et al. [4], however, considered the possibility of complex formation with the ubiquitous and abundant carbonate species. This is rather surprising, as there are clear indications that Zr forms strong carbonate complexes and there are even published values for stability constants. For instance, dissolution experiments with the mineral weloganite (a Na–Zr–Sr hydrous carbonate), yielded high equilibrium Zr concentrations (about $10^{-4}$ M at pH $\sim$ 8, see Ref. [6]). In addition, João et al. [8] were able to prepare stable solutions with Zr concentrations of $\sim 10^{-3}$ M in the presence of 0.5–1 M total carbonate (at pH 10). Finally, spectroscopic studies indicate unequivocally the existence of Zr-carbonate complexes [9].

There is, however, considerable disagreement about the stoichiometry of Zr–carbonate complexes. João et al. [8] interpreted their data assuming that the mononuclear tetrameric species $Zr(CO_3)_4^{4-}$ forms, whereas Karlysheva et al. [9] assumed the existence of a ternary complex, $Zr(OH)_2(CO_3)^0$, in addition to the dimeric species $Zr(CO_3)_2^0$. Since both studies were conducted under comparable conditions (in terms of carbonate concentrations and ionic strength) such inconsistencies in the interpretation appear suspect and one should not take the identity of the proposed species for granted. Unfortunately, both publications are very condensed and

the raw laboratory data needed to check the results are not reported.

João et al. [8] determined an equilibrium constant for the reaction:

$$Zr(OH)_2^{2+} + 4CO_3^{2-} \leftrightarrows Zr(CO_3)_4^{4-} + 2OH^-$$
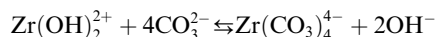
and obtained log $K = 39.95$. Their determination is based on the comparison of the Zr–CO$_3$ complexation reaction with a competing reaction involving a concurrent ligand (Zr–EDTA). Unfortunately, they erroneously assumed that the dominant species produced through hydrolysis is $Zr(OH)_2^{2+}$. An inspection of the formal derivation of the constant reported above also showed that the formation of the mixed complexes $Zr(OH)EDTA^-$ and $(Zr(OH)EDTA)_2^{2-}$ was neglected (see Ref. [10], vol. 1, p. 207). Thus, even if their work offers important clues about the existence of strong Zr–carbonate complexes, it is not possible to use this constant for speciation calculations.

### 3.3. Estimation of formation constants for Zr–carbonate complexes

In view of the inconsistencies discussed above, an attempt will be made to determine stability constants for Zr–carbonate complexes via chemical analogues. Such estimation techniques are becoming increasingly important in view of the scarcity of reliable thermodynamic data (see ch. 3 in Ref. [11]).

Considering that no reliable data on the complexation of Ti(IV), Hf(IV) and Ce(IV) with carbonate exist, the best available analogues of Zr(IV) are the tetravalent actinides. The analogy between tetravalent actinides and Zr(IV) is suggested by identical redox states, similar electronegativities ($Zr^{4+} = 1.3$, $Th^{4+}$–$Pu^{4+} = 1.3$–$1.7$ on the Pauling scale) and marked similarities in chemical behaviour (both Zr and tetravalent actinides are strong Lewis acids and undergo strong hydrolysis, in addition both form hydrous carbonates). The ionic radii, however, differ considerably, the $Zr^{4+}$ ion being about 20% smaller than the tetravalent actinide cations ($Zr^{4+} = 0.72$ Å, $An^{4+} = 0.8$–$0.94$ Å for CN = VI [12]), which could lead to significant differences in the coordination chemistry of these metal ions (see later).

In order to estimate the strength of Zr–carbonate complexes, we therefore analyzed the available data on actinide(IV)–carbonate complexes. Particularly for Th, there are two independent investigations on complex formation with carbonate [13,14]. These data indicate that the increase in Th concentration observed in carbonate-rich solutions is best modeled assuming the formation of a pentahydroxide, $Th(CO_3)_5^{6-}$, and of a mixed complex, $Th(OH)_3CO_3^-$.

Stability constants have been determined also for the U(IV) and Pu(IV)–pentacarbonate complexes (see compilation in Ref. [15]). It appears that within the
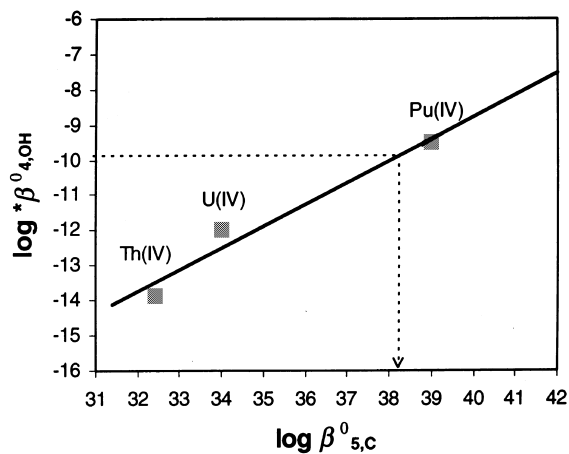


Fig. 1. Correlation between formation constants of tetrahydroxide and pentacarbonate complexes for three actinides (see Table 1 for definition of the constants). Data are taken from the compilation of Berner [15] (Table 9 in cited reference). From the linear regression a value of $10^{38.2}$ is derived for the formation constant of $Zr(CO_3)_5^{6-}$ using the Zr(IV) hydrolysis data given in Table 1.

series of tetravalent actinides the stability of carbonate complexes increases with decreasing ionic radius. The value of the formation constant of the pentacarbonate complex increases in the sequence $Th^{4+}$ (0.94 Å), $U^{4+}$ (0.89 Å) $Pu^{4+}$ (0.86 Å) from $\log\beta_{5,C}^0 = 32.3$ to 39.0 (see Fig. 1 and Table 1 for constant definitions), reflecting the increasingly electrophilic character of these ions. The same trend can be observed for the first and particularly for the fourth hydrolysis constants, which also increase in the sequence $Th^{4+}$–$U^{4+}$–$Pu^{4+}$.

Fig. 1 shows, for the mentioned actinides, a cross correlation between the stability constants of the pentacarbonate and tetrahydroxide complexes. Using $\log{}^*\beta_{4,OH}^0 = -9.7$ for the fourth Zr hydrolysis constant (see Table 1) it is then possible to extrapolate a value of $10^{38.2}$ to for the Zr–pentacarbonate complex (arrow in Fig. 1). This value is close to the formation constant of Pu(IV)-pentacarbonate ($10^{39}$). Considering the uncertainties involved in such extrapolations, it seems reasonable to use, conservatively, $10^{39}$ rather than $10^{38.2}$ as best estimate for the stability constant of the Zr–pentacarbonate complex. It must be however pointed out that the value reported in Fig. 1 for the stability constant of Pu(IV)–pentacarbonate is itself derived from an estimation procedure based on partly conflicting data and is possibly too high (see ch. 7 in Ref. [15]).

Thus, although our estimation procedure indicates that Zr–carbonate complexes are stronger than the corresponding Th complexes, it is difficult to define a reliable upper limit and further substantiating data are required. Evidence supporting our prediction that Zr–carbonate complexes are stronger than those of Th

Table 1
Summary of equilibria and constants used to calculate the solubility of monoclinic zirconia [a]

| Reaction | Equilibrium constant | Source |
|---|---|---|
| *Primary equilibria* | | |
| (a) $CO_2(g) + H_2O = H_2CO_3^0$ | $\log K_1 = -1.47$ | Ref. [17] |
| (b) $H_2CO_3^0 = HCO_3^- + H^+$ | $\log K_2 = -6.4$ | Ref. [17] |
| (c) $HCO_3^- = CO_3^{2-} + H^+$ | $\log K_3 = -10.3$ | Ref. [17] |
| (d) $m\text{-}ZrO_2 + 4H^+ = Zr^{4+} + 2H_2O$ | $\log K_{s,0}^0 = -1.9$ | Ref. [5] |
| (e) $Zr^{4+} + 5H_2O = Zr(OH)_5^- + 5H^+$ | $\log {}^*\beta_{5,OH}^0 = -16.0$ | Ref. [5] |
| (f) $Zr^{4+} + 5CO_3^{2-} = Zr(CO_3)_5^{6-}$ | $\log \beta_{5,C} = 32.3$ to $42.0$ | Ref. [13] [b] |
| (g) $Zr^{4+} + 3H_2O + CO_3^{2-} = Zr(OH)_3CO_3^- + 3H^+$ | $\log \beta_M = -0.53$ to $1.95$ | Ref. [13] [b] |
| (h) $H_2O = H^+ + OH^-$ | $\log K_0^w = -14.0$ | Ref. [17] |
| *Auxiliary equilibria* | | |
| (i) $Zr(OH)_5^- + 5H^+ + 5CO_3^{2-} = Zr(CO_3)_5^{6-} + 5H_2O$ | $\log {}^*\beta_{5,C}^0 = 48.3$ to $58$ | – |
| (j) $m\text{-}ZrO_2 + 3H_2O = Zr(OH)_5^- + H^+$ | $\log K_{s,5}^0 = -17.9$ | – |
| (k) $Zr(OH)_5^- + 2H^+ + CO_3^{2-} = Zr(OH)_3CO_3^- + 2H_2O$ | $\log {}^*\beta_M^0 = 15.5$ to $18.0$ | – |
| *Additional hydrolysis equilibria* | | |
| (l) $Zr^{4+} + 4H_2O = Zr(OH)_4^0 + 4H^+$ | $\log {}^*\beta_{4,OH}^0 = -9.7$ | Ref. [5] |

[a] All constants are extrapolated at zero ionic strength and refer to 298 K. The constants for the auxiliary equilibria were obtained through linear combinations of the primary equilibria. The last equilibrium equation, which defines the formation of the fourth Zr-hydroxide complex, is used to estimate the formation constant of Zr–pentacarbonate complex.

[b] This reference applies only to the lower limit of the given ranges. The upper limits are estimated maximum values (see text).

comes from an independent estimation procedure [16], based on an empirical correlation among the stability constants of Zr and Th complexes formed with both organic and inorganic ligands (Fig. 2). The constants are linearly correlated, yielding the regression

$$\log K_{1(Zr\ complex)} = 1.1(\pm 1.5)$$
$$+ 1.15(\pm 0.07)\log K_{1(Th\ complex)}.$$

From this equation one obtains $\log \beta_{5,C}^0 = 38.2 \pm 3.8$ as stability constant for $Zr(CO_3)_5^{6-}$, using $\log K_{(Th\ complex)} = 32.3$ for $Th(CO_3)_5^{6-}$. Since the previous extrapolation based on the correlation between hydrolysis and carbonate stability constants of tetravalent actinides also yielded $\log \beta_{5,C}^0 = 38.2$, the two estimation methods are remarkably consistent. Therefore, we will use the upper limit of the latter estimation ($\log \beta_{5,C}^0 = 38.2 + 3.8 = 42$) to estimate the maximum effect of Zr–pentacarbonate on the solubility of zirconia.

Although the empirical correlation shown in Fig. 2 refers to monomeric species, it has been shown that such linear correlations may be conserved at least up to trimeric complexes. For instance, the stability constants for the formation of monomeric, dimeric and trimeric complexes of many metals with oxalate are reciprocally correlated (see Fig. III.37 in Ref. [11]). This relation is particularly noteworthy considering the resemblance in chemical composition and geometry of carbonate and oxalate groups (both form bidentate complexes attached to C–O bonds).

In addition, one has to consider that the complexes formed with chelating ligands, like EDTA, CDTA and
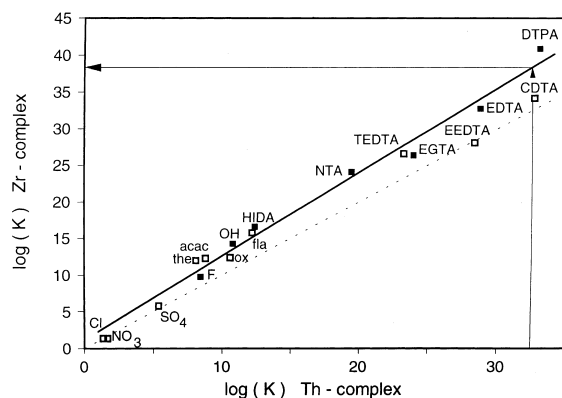
Fig. 2. Stability constants of monomeric complexes with $Th^{4+}$ and $Zr^{4+}$ (adapted from Ref. [16]). The solid line represents the linear best fit calculated from the most reliable data (■), while the broken line indicates unity slope (equal values for Th and Zr constants). Abbreviations for organic ligands are: the: thenoyltrifluoroacetone; acac: acetylacetone; ox: oxalate; fla: flavonol-2′-sulfonic acid; HIDA: N-(2-hydroxyethyl)iminodiacetic acid; NTA: nitrilotriacetic acid; TEDTA: thiobis(ethylenenitrilo)tetraacetic acid; EGTA: ethylenebis(oxyethylenenitrilo) tetraacetic acid; EDTA: ethylenediamminetetraacetic acid; EEDTA: oxybis(ethylenenitrilo) tetraacetic acid; CDTA: trans-1,2-cyclohexylenedinitrilotetraacetic acid; DTPA: diethylenetrinitrilopentaacetic acid.

DPTA, are polydentate and thus bear some analogy with polymeric complexes formed with smaller monodentate or bidentate ligands. The fact that the estimated Zr–pentacarbonate constant falls close to the stability

constants of these polydentate organic complexes is thus a further indication that our extrapolation procedure is meaningful.

### 3.4. Stoichiometry of Zr–carbonate complexes

Direct spectroscopic evidence for the stoichiometry and coordination of the actinide(IV)–carbonate complexes exists in the case of Th [14]. EXAFS analyses indicate that a highly charged bidentate $Th(CO_3)_5^{6-}$ complex effectively exists at bicarbonate concentrations above 0.1 M. At lower concentrations, the Th–O distances shrink and the coordination number decreases from 10 to 8 oxygens, suggesting the formation of a mixed hydroxide–carbonate complex.

Considering that bicarbonate concentrations in the repository environment will not exceed 0.1 M and in view of the smaller ionic radius of $Zr^{4+}$, the existence of an analogous species with stoichiometry $Zr(CO_3)_5^{6-}$ and bidentate binding cannot be taken for granted. Specifically, one may ask whether a coordination by 10 oxygens is still possible for the significantly smaller $Zr^{4+}$. The formation of a Zr complex coordinated by five carbonate groups appears possible if monodentate binding is assumed (since carbonate groups are planar, steric hindrance problems should be minor in the case of monodentate binding).

In spite of all these uncertainties, the use of the proposed constants for the formation of $Zr(CO_3)_5^{6-}$ can be justified if it is taken as a purely empirical tool for a conservative estimate of the $ZrO_2$ solubility in the presence of carbonate. The proposed stoichiometry should not be taken to reflect a real species, but as a useful formalism to enable a rough, but consistent modeling of Zr–carbonate complexation.

### 3.5. Model development

A simplified speciation model based on the data compiled in Table 1 has been developed in order to calculate the solubility of monoclinic zirconia as a function of the master variables pH, carbon dioxide partial pressure ($pCO_2$) and ionic strength ($I$).

The model applies to the conditions prevailing in a typical high-level waste repository environment as described before and therefore cannot be extended beyond a specific parameter range. Its validity is restricted to the pH range 7–9, $pCO_2 < 1$ kPa and ionic strengths not exceeding 0.1 M.

For the conditions specified above, the total Zr concentration in solution is given by the sum of the molal concentrations of the dominating species $Zr(OH)_5^-$, $Zr(CO_3)_5^{6-}$, and $Zr(OH)_3CO_3^-$:

$$m_{Zr} = m_{Zr(OH)_5^-} + m_{Zr(CO_3)_5^{6-}} + m_{Zr(OH)_3CO_3^-}. \quad (1)$$

From equilibria (i), (j) and (k) in Table 1 we obtain

$$m_{Zr(OH)_5^-} = \frac{K_{s,5}^0}{\gamma_{Zr(OH)_5^-} \cdot a_{H^+}}, \quad (2)$$

$$m_{Zr(CO_3)_5^{6-}} = {}^*\beta_{5,C}^0 \cdot m_{Zr(OH)_5^-} \cdot m_{CO_3^{2-}}^5 \cdot a_{H^+}^5$$
$$\cdot \frac{\gamma_{Zr(OH)_5^-} \cdot \gamma_{CO_3^{2-}}^5}{\gamma_{Zr(CO_3)_5^{6-}}}, \quad (3)$$

$$m_{Zr(OH)_3CO_3^-} = {}^*\beta_M^0 \cdot m_{Zr(OH)_5^-} \cdot m_{CO_3^{2-}} \cdot a_{H^+}^2$$
$$\cdot \frac{\gamma_{Zr(OH)_5^-} \cdot \gamma_{CO_3^{2-}}^2}{\gamma_{Zr(OH)_3CO_3^-}}, \quad (4)$$

where the symbols $a_i$ and $\gamma_i$ denote activity and activity coefficient of the species $i$, respectively. The molality of the carbonate ion is obtained by combining equilibria (a), (b) and (c):

$$m_{CO_3^{2-}} = K_1 \cdot K_2 \cdot K_3 \cdot \frac{pCO_2}{a_{H^+}^2 \cdot \gamma_{CO_3^{2-}}}. \quad (5)$$

Setting $K_\alpha \equiv K_1 \cdot K_2 \cdot K_3$, substituting Eqs. (2) and (5) into Eqs. (3) and (4), and finally substituting back into Eq. (1) one obtains

$$m_{Zr} = \frac{K_{s,5}^0}{a_{H^+} \cdot \gamma_{Zr(OH)_5^-}} + \frac{{}^*\beta_{5,C}^0 \cdot K_{s,5}^0 \cdot (K_\alpha)^5 \cdot (pCO_2)^5}{a_{H^+}^6 \cdot \gamma_{Zr(CO_3)_5^{6-}}}$$
$$+ \frac{{}^*\beta_M^0 \cdot K_{s,5}^0 \cdot K_\alpha \cdot pCO_2 \cdot \gamma_{CO_3^{2-}}}{a_{H^+} \cdot \gamma_{Zr(OH)_3CO_3^-}}, \quad (6)$$

which is a function of the carbon dioxide partial pressure and pH. The activity coefficients have been evaluated using Davies' approximation [17]:

$$\log \gamma_i = -A \cdot z_i^2 \cdot \left( \frac{\sqrt{I}}{1 + \sqrt{I}} - 0.2I \right), \quad (7)$$

where $A = 0.51$ (at 298 K), $z_i$ is the ion charge and $I$ the ionic strength.

### 3.6. Composition of the pore solution in contact with the waste

The chemistry of a solution in contact with radioactive waste in a deep repository will be largely determined by the composition of the groundwater accessing the repository and by equilibration reactions with the engineered barriers surrounding the waste.

Reference solution compositions have been modeled for the high-level waste repository planned in Switzerland (see Table 19 in Ref. [18]). A typical reference water is reported in Table 2 and will serve as a base to evaluate the solubility of zirconia in the repository environment. Other compositions are not considered in view of the uniformity of such waters in terms of ionic strength, pH and carbonate content.

Table 2
Chemical composition and additional parameters for the reference pore water used to predict the solubility of zirconia in the repository environment (water CRW_2A, see p. 60 in Ref. [18])

| | |
|---|---|
| $T$, K | 323 |
| pH | 9.0 |
| $I$, M | 0.08 |
| log $pCO_2$, kPa | −0.55 |

| Element | Total concentration, M |
|---|---|
| Na | $7.8 \times 10^{-2}$ |
| K | $1.7 \times 10^{-4}$ |
| Mg | $6.7 \times 10^{-5}$ |
| Ca | $1.1 \times 10^{-5}$ |
| Al | $1.0 \times 10^{-4}$ |
| Si | $2.6 \times 10^{-4}$ |
| TIC (carbonate) | $5.2 \times 10^{-2}$ |
| Cl | $3.0 \times 10^{-3}$ |

### 3.7. Solubility of zirconia under repository conditions

The results of the model calculations carried out with the speciation model developed above are presented graphically in Fig. 3. These calculations were verified by complete speciation calculations performed with the MINEQL/PSI geochemical code, which included all species listed in the reference water composition reported in Table 2.

The plot in Fig. 3 indicates that a significant increase in $ZrO_2$ solubility due to the formation of carbonate complexes will occur only at carbon dioxide partial pressures larger than $10^{-1.5}$ kPa (this value corresponds to normal atmospheric conditions). Taking into account
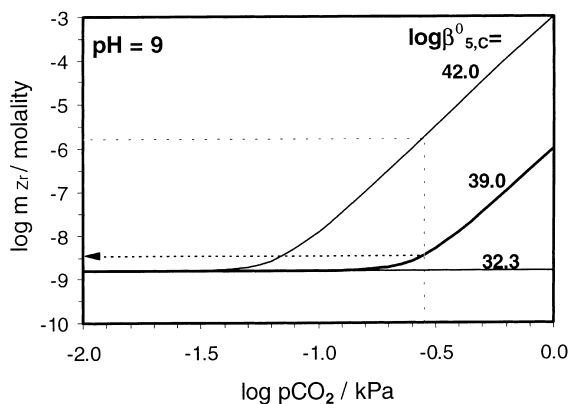
the pH and $pCO_2$ values prevailing in the reference pore water (Table 2), our calculations predict as maximum effect an increase of the solubility of zirconia up to $\sim 10^{-6}$ M. However, using the best estimate for the stability constant of $Zr(CO_3)_5^{6-}$ ($\log {}^*\beta_{5,C}^0 = 39$) a much smaller effect is predicted, and in this case the solubility would remain at a very low level (less than $10^{-8}$ M).

An increase in solubility approaching the millimolar range, although unlikely, cannot be ruled out completely, considering that carbon dioxide partial pressures in the order of 1 kPa (at pH 8–9) have already been determined for waters collected from potential repository environments [19]. The precision of our estimation for the formation constant of $Zr(CO_3)_5^{6-}$ is evidently insufficient to carry out reliable predictions at high $pCO_2$ (our predictions span six orders of magnitude at $pCO_2 = 1$ kPa) and only careful experimental work could resolve this problem.

According to our calculations, within the pH range and ionic strength of interest the Zr speciation in bentonite pore water would be dominated by $Zr(OH)_5^-$ and $Zr(CO_3)_5^{6-}$ and the mixed complex $Zr(OH)_3CO_3^-$ will play in any case a minor role. Fig. 4 shows a typical speciation for conditions relevant in a repository environment.

## 4. Comparison with borosilicate glasses and spent fuel

Borosilicate glass is the conventional matrix for reprocessed high-level radioactive waste. Vitrified waste forms are being already produced on industrial scale and therefore there is an enormous body of experimental data dealing with the stability of this material in a repository environment. Although glass has no thermodynamic solubility product like a crystalline compound, an operational 'solubility' can be defined, which corre-
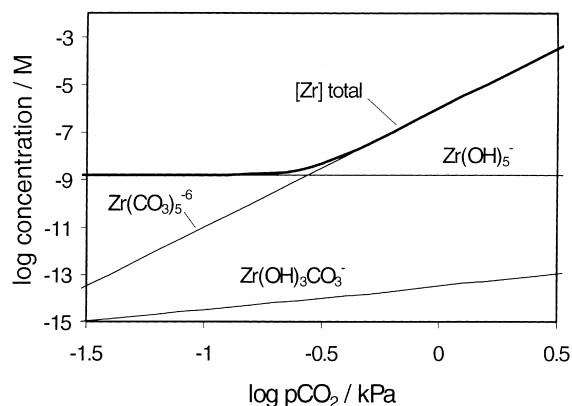


Fig. 3. Predicted effect of carbonate complexes on the solubility of zirconia at pH 9 and $I = 0.08$ M. For a carbon dioxide partial pressure equal to that predicted for our model repository environment ($10^{-0.55}$ kPa), the increase in solubility would be less than one order of magnitude with $\log \beta_{5,C}^0 = 39$ (best estimate), while concentrations approaching $10^{-6}$ M are predicted with $\log \beta_{5,C}^0 = 42$ (maximum effect).



Fig. 4. Zr speciation in equilibrium with monoclinic zirconia as a function of the carbon dioxide partial pressure (calculated for pH = 9, $I = 0.08$ M, $\log {}^*\beta_{5,C}^0 = 39$, $\log {}^*\beta_M^0 = -0.53$).

sponds to a steady state concentration of dissolved silica attained when the dissolution rate of the glass approaches a limiting minimum value. This Si concentration is frequently close to $10^{-3}$ M [20]. Compared with our best estimate for the solubility of zirconia under repository conditions ($\sim 10^{-9}$–$10^{-8}$ M), this implies that a vitrified waste matrix will be five orders of magnitude more soluble.

Conventional spent fuel is mainly composed of $UO_2$, with or without a contribution of $PuO_2$ (MOX-elements). Due to the redox-sensitivity of U and Pu, the solubility of spent fuel is highly dependent on the oxidation potential prevailing in the repository environment. Final repositories for high-level waste are usually designed in such a way to guarantee reducing conditions. Under such circumstances, the solubilities of Pu and U oxides are orders of magnitude lower than under oxidising conditions. Berner [15] gives realistic solubility limits of $10^{-7}$ M for U(IV) and $10^{-8}$ M for Pu(IV) in the reference pore waters for the Swiss repository, based on a review of the available thermodynamic data. These numbers do not differ greatly from the predicted $ZrO_2$ solubility. This is not surprising in view of the procedure adopted to estimate the complexation of Zr with carbonate, which was based on the chemical analogy between Zr and tetravalent actinides and on the similarity of the hydrolysis constants.

As far as the dissolution kinetics of zirconia is concerned, a comparison with borosilicate glass is difficult due to the scarcity of adequate tests, as all leaching experiments with zirconia have been conducted over a time span not exceeding a few weeks. Consequently, these data yield short-term leaching rates, which are as a rule much higher than rates measured over one or more years.

Recent experiments suggest, for a monoclinic $ZrO_2$–SrO solid solution leached during 15 days in deionized water (370 K, pH 9), rates in the order of $10^{-2}$–$10^{-3}$ g $m^{-2}$ $d^{-1}$ [21]. Other leaching tests lasting 56 days [22] indicate rates between 1 and $6 \times 10^{-4}$ g $m^{-2}$ $d^{-1}$ for coupons of fully stabilised cubic zirconia in contact with high-salinity solutions ($T = 298$–$358$ K). Finally, leach rates of $\sim 10^{-6}$–$10^{-5}$ g $m^{-2}$ $d^{-1}$ have been determined for Y-stabilised cubic zirconia in deionised water at 363 K, pH 5.6 and after 30 days leaching time [23].

Initial dissolution rates normally measured for borosilicate glasses in deionised water are close to 1 g $m^{-2}$ $d^{-1}$, i.e. at least two orders of magnitude higher than for zirconia. After sufficient leaching time, however, borosilicate glass leaching rates decrease to $\sim 10^{-3}$–$10^{-4}$ g $m^{-2}$ $d^{-1}$ at 363 K due to the release of silica into solution (saturation effect, see [20]). Thus, among the currently available leach test data for zirconia only those of Kamizono et al. [23] unequivocally indicate a higher durability than borosilicate glass. Further tests are thus needed to study the kinetics of $ZrO_2$ dissolution as a function of time and saturation. Specifically, a study

should be undertaken to verify whether the dissolution rates of $ZrO_2$ decrease in a similar way as those of borosilicate glass when saturation is approached.

## 5. Conclusions and recommendations

Our analysis, based on available and estimated thermodynamic data, indicates that zirconia should remain relatively insoluble in a repository environment, in spite of the formation of carbonate complexes. However, the equilibrium constants used to predict the solubility of monoclinic zirconia are affected by large uncertainties, particularly in the pH range of interest. This leads to conservative estimations of Zr equilibrium concentrations in a typical repository environment approaching $10^{-6}$ M, i.e. at least two orders of magnitude above our best estimate ($\sim 10^{-9}$–$10^{-8}$ M). These predictions cannot be substantiated by experimental data, since – to the author's knowledge – no laboratory determination of the solubility of m-$ZrO_2$ in the near-neutral region has been carried out up to date.

Although the available kinetic data indicate that zirconia is much more durable than borosilicate glasses, they are inconclusive, as long-term leaching tests on zirconia have not been carried out.

Under such circumstances, it is advisable to carry out further experiments aiming at determining both solubility and long-term dissolution kinetics of zirconia (both in the stabilised cubic and in the monoclinic form) at the conditions of interest. Due to the very low equilibrium concentrations expected, these determinations should be carried out with the help of radioactive tracers (ideally $^{95}$Zr). A series of long-term leaching tests similar to those conducted on glass specimens (see e.g. [24]) should be carried out to elucidate the long-term kinetic behavior of zirconia.

## References

[1] C. Degueldre, U. Kasemeyer, F. Botta, G. Ledergerber, Mater. Res. Soc. Symp. Proc. 412 (1996) 15.
[2] G. Ledergerber, C. Degueldre, A. Stanculescu, J.M. Paratte, in: Proceedings of the International Conference on Future Nuclear Systems, Global '97, Yokohama, Japan, 5–10 October 1997, JAERI, 1998, pp. 1068–1073.

[3] NAGRA, Kristallin I – Safety assessment report, Technical Report NTB 93-22, NAGRA, Wettingen, Switzerland, 1995.

[4] J.H. Adair, R.P. Denkewicz, F.J. Arriagada, Ceram. Trans. 1 (1987) 135.

[5] C.F. Baes, R.E. Mesmer, The Hydrolysis of Cations, Krieger, FL, 1986.

[6] S.U. Aja, S.A. Wood, A.E. Williams-Jones, Appl. Geochem. 10 (1995) 603.

[7] H. Remy, Lehrbuch der anorganischen Chemie, 5th ed., Akademische Verlagsgesellschaft Geest and Portig K.-G., Leipzig, 1949.

[8] A. João, S. Bigot, F. Fromage, Bull. Soc. Chim. France 1987 (1987) 943.

[9] K.F. Karlysheva, L.S. Chumakova, L.A. Malinko, I.A. Sheka, Russ. J. Inorg. Chem. 27 (1982) 1582.

[10] R.M. Smith, A.E. Martell, Critical Stability Constants: Amino Acids, Plenum, New York, 1974.

[11] I. Grenthe, W. Hummel, I. Puigdomenech, in: I. Grenthe, I. Puigdomenech (Eds.), Modelling in Aquatic Chemistry, Nuclear Energy Agency, Paris, 1997, pp. 69–129.

[12] R.D. Shannon, Acta Crystallogr. A 32 (1976) 751.

[13] E. Östhols, J. Bruno, I. Grenthe, Geochim. Cosmochim. Acta 58 (1994) 613.

[14] A.R. Felmy, D. Rai, S.M. Sterner, M.J. Mason, N.J. Hess, S.D. Conradson, J. Sol. Chem. 26 (1997) 233.

[15] U. Berner, KRISTALLIN I: Estimates of solubility limits for safety relevant radionuclides, PSI Report Nr. 95-07, Paul Scherrer Institute, Villigen, Switzerland and Technical Report NTB 94-08, NAGRA, Wettingen, Switzerland, 1995.

[16] W. Hummel. Thermodynamic data base for organic ligands, Technical Report TM-41-91-43, Paul Scherrer Institute, Villigen, Switzerland, 1992, available on request.

[17] W. Stumm, J.J. Morgan, Aquatic Chemistry, 3rd ed., Wiley, New York, 1996.

[18] E. Curti, Modelling bentonite pore waters for the Swiss high-level radioactive waste repository, PSI Report Nr. 93-05, Paul Scherrer Institut, Villigen, Switzerland and Technical Report NTB 93-45, NAGRA, Wettingen, Switzerland, 1993.

[19] F.J. Pearson, Jr., J.L. Localma, A. Scholtis, Chemistry of waters in the Böttstein, Weiach, Riniken, Schafisheim and Leuggern boreholes: a hydrochemically consistent data set, Technical Report NTB 86-19, NAGRA, Wettingen, Switzerland, 1989.

[20] E.Y. Vernaz, J.L. Dussossoy, Appl. Geochem. (Suppl. 1) (1992) 13.

[21] N.C. Dutta, Radiochim. Acta 79 (1997) 25.

[22] R. Heimann, T.T. Vandergraaf, J. Mater. Sci. Lett. 7 (1988) 583.

[23] H. Kamizono, I. Hayakawa, S. Muraoka, J. Am. Ceram. Soc. 74 (1991) 863.

[24] E. Curti, Modelling the dissolution of borosilicate glasses for radioactive waste disposal with the PHREEQE/GLAS-SOL code: theory and practice, PSI-report Nr. 86, Paul Scherrer Institut, Villigen, Switzerland, and Technical Report NTB 91-08, NAGRA, Wettingen, Switzerland, 1991.