AQUEOUS SOLUBILITY OF ZIRCONIA

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Zirconia (zirconium dioxide) is being considered as a host matrix for the disposal of actinides in a geologic disposal vault, for the "burning of actinides" in nuclear reactors and for the use of lanthanides as burnable-neutron absorbers to control the neutron flux in the reactors. These applications require knowledge of the stability of the zirconia in aqueous environment. Therefore, a literature review of the aqueous solubility of zirconia was carried out. The literature review was complemented by experiments on the dissolution of zirconia in aqueous solutions. The paper presents the results of the literature review and our experiments on the dissolution of zirconia in solutions of pH between 5.7 and 10.3. The low solubility of zirconia in the solutions investigated here supports the selection of zirconia for the above applications.

1. Introduction

Zirconia (zirconium dioxide ZrO_2) is being considered as a potential host matrix to dispose the actinide waste produced during fuel reprocessing [1,2]. Also, zirconia has been suggested as the host matrix for the burning of excess plutonium and of minor actinides (Np, Am and Cm) in nuclear reactors [3]. The problem of the disposal of the excess plutonium and minor actinides (MA) would become important if fuel recycling is carried out to extend the fuel supply. Recently, the use of zirconia as a host matrix for burnable nuclear absorbers (BNA), such as dysprosium and gadolinium, has been proposed to control the neutron flux in a reactor [4]. Zirconia is a good choice for these applications as it can incorporate actinides and lanthanides in its lattice. These in-reactor applications also make use of the fact that zirconia is non-reactive, is stable at high temperatures, has a low neutron absorption cross-section and has a low solubility in water. Analysis of the performance of "zirconia-matrix materials" in a reactor requires an understanding of the release of the element presents in the zirconia matrix into the reactor coolant in case of a defect in the cladding. Hence, there is a need to know the solubility of zirconia and the elements present within the zirconia matrix if zirconia is to be used for the applications described above.

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The pH of coolant in a CANDU type reactor is about 10 [5]. The pH of the groundwater, at the depth of the geologic disposal vault envisaged in the Canadian Nuclear Fuel Waste Management Program, is between 6 and 9 [6]. Therefore, the aim of this work is to obtain information about the solubility of zirconia in water for pH conditions relevant to the nuclear applications of zirconia described above. This paper summarizes the results of a literature review on the solubility of zirconia. Leaching tests to determine the solubility of zirconia were carried out to fill in the gaps in the information about its solubility for the nuclear applications described above.

2. Literature Review

Despite the important role of zirconia in the potential nuclear applications, its behaviour in aqueous solutions has not received the attention it needs. Although the solubility of zirconia has been studied theoretically and experimentally by several groups [1,2,6-22], the reported results have been contradictory. The existing literature on the solubility of zirconia was reviewed and the results of the review are briefly summarized here. The first section focuses on zirconium(IV) hydrolysis products in solution and the second section discusses previous solubility experiments and models.

2.1 Hydrolysis of zirconium(IV)

The aqueous chemistry of zirconium(IV) is dominated by the complexation of Zr^{4+} with hydroxide ions. At low zirconium concentrations, and in acidic solutions (i.e., pH < 1) mononuclear hydrolysis species, $Zr(OH)_h^{(4-h)+}$ are formed [7]. Increasing the zirconium concentration results in the formation of poly-nuclear species. The corresponding stability constants, $\beta_{m,h}$, are related to the general equilibrium:

$$mZr^{4+} + hH_2O = Zr_m(OH)_h^{(4m-h)+} + hH^+ \tag{1}$$

$$\beta_{m,h} = \frac{\left[Zr_m(OH)_h^{(4m-h)+}\right]\left[H^+\right]^h}{\left[Zr^{4+}\right]^m} \tag{2}$$

The stoichiometries of the primary species in solution as well as their corresponding stability constants have been the source of some debate and many discrepancies exist in the literature. Furthermore, experimental data has largely been confined to the strongly acidic or strongly basic pH regions. Some studies have used experimentally determined stability constants to extrapolate zirconium solubility to the intermediate pH region [7-10]. Recently, Brown *et al.* [19] have critically reviewed all the published literature on the thermodynamics of zirconium and its compounds published till 2002. References 7, 9 and 14 also provide excellent literature reviews of zirconium oxide solubility but the review by Brown *et al.* is the most comprehensive.

2.2 Zirconia Solubility

The solubility of zirconia in the intermediate pH range has received little attention. As previously mentioned, most experimental data is restricted to the pH extreme (see Bilinski *et al*. [16], Kovalenko and Bagdarasov [20], Michel [21] and Sheka and Pevner [17]). Zirconia solubility, determined experimentally by Ekberg *et al*. [9] in 1 M ($H,Na(ClO_4)$), as a function of pH is shown in Figure 1. The data point obtained by Pouchon [8] at pH 9 is also shown in this figure.

Some other estimates of zirconia solubility are also available in the literature. For instance, according to Gong *et al*. [2], based on thermodynamic calculations, zirconia has a low solubility of $<10^{-10}$ M with little temperature dependence (citing Heimann and Vandergraff [1]). Tromans [19] has calculated the solubility of zirconia at 25ºC and 150ºC, both as a function of pH and of amorphism in the solid, using thermodynamic data. His results indicate that, in the near neutral solutions, temperature has little effect on the solubility of crystalline zirconia. There is a small shift in the solubility minima to lower pH value in going from 25ºC to 150ºC. Tromans attributes the shift in the minima to a decrease in the neutrality pH of water - from 6.9985 at 25 ºC to 5.825 at 150ºC [19]. However, his results show significant temperature effect on zirconia solubility at pH = 10, the pH value close to that of the CANDU coolant. According to Tromans, zirconia solubility increases by about an order of magnitude if temperature increases from 25ºC to 150ºC.

Relevant solubility limits for zirconia published in the literature for the pH region of interest are summarised in Table 1 according to the information available to us. The zirconia solubility limits range from as low as 10^{-11} M to as high as 10^{-7} M. The large range highlights the need for additional experimental data.

Table 1 Comparison of the published zirconia solubilities*

Solubility, M	**Conditions**	**Nature of value**	**Reference**	**Year**
10^{-11}-10^{-9}	pH 7-9,	Calculated based on stability constants	[10] Adair *et al.*	1988
10^{-9}-10^{-8}	pH 7-9	Calculated based on stability constants	[15] Curti and Hummel	1999
$<10^{-10}$		Calculated	[2] Gong *et al.* based on Heimann [1]	2000
$(5.5 \pm 0.6) \times 10^{-9}$	pH 9	Obtained experimentally via leaching tests	[8] Pouchon *et al.*	2001
8.9×10^{-8}	pH 7 1 M $NaClO_4$	Obtained experimentally via leaching tests	[9] Ekberg *et al.*	2004
7.8×10^{-8}	pH 11 1 M $NaClO_4$	Obtained experimentally via leaching tests	[9] Ekberg *et al.*	2004
3.3×10^{-8}	pH 10.00	Calculated	[19] Tromans	2006
4.3×10^{-7}	pH 10.00 423 K	Calculated	[19] Tromans	2006

*Data for room temperature, unless stated otherwise

The extent of amorphism has significant effect on the solubility of zirconia according to the calculations of Tromans [19]. Therefore, it would be prudent that all studies on the leaching of zirconia (and doped-zirconia) should be carried out using well-characterized samples. Samples used in these tests should be characterized not only for their chemical composition but also for their crystallinty.

3. Experimental

3.1 Materials

The zirconium oxide powder (anhydrous) was obtained from Fisher Scientific (Lot # 733489). The sample was characterized using several surface analytical techniques. The phase of the sample was determined by X-ray diffraction (XRD). The XRD spectrum is shown in Figure 2. The XRD spectrum shows the sample of zirconium oxide powder to be monoclinic [23].

The Scanning Electron Microscopy (SEM) images showed the powder to consist of small particles (on the order of 1-10 μm in diameter), which were not uniform in size, Figure 3. Particle size analysis performed using laser scattering revealed an average particle size of 8.3 μm without the sonication of the sample and of 4.9 μm after sonication for 5 minutes. The surface area of the sample was calculated using the average particle size as determined by light scattering after 5 minutes sonication. A hard sphere model was assumed. The surface area of the sample was calculated to be 0.21 m^2/g.

Sample impurity was determined using Inductively Coupled Plasma- Mass Spectrometry (ICP-MS) and Energy Dispersive X-ray (EDX) analysis. ICP-MS analysis revealed a significant hafnium impurity (approximately 2 wt% Hf) as well as small titanium and aluminium impurities. The EDX spectrum showed Zr and O peaks as well as a very small Al peak.

3.2 Method

The tests were performed using 250 mL Erlenmeyer flasks. The tare weight of each flask was measured and recorded. Roughly 2 g of the oxide powder was added to each flask followed by 200 mL of the solvent. The start date and time was recorded at this point. The flask was briefly swirled with a gentle motion. Table 2 gives the list of the tests carried out in this study.

The solution pH of each flask was measured and recorded (“Initial pH” in Table 2). The headspace of each flask was purged with argon. The headspace was allowed to purge for a minimum of five minutes in order to displace carbon dioxide gas. The flask was immediately sealed with Parafilm. Flasks were placed in a sandbath in an attempt to minimize temperature fluctuations. The temperature of the sandbath was monitored using a mercury thermometer. Room temperature was 298 ± 5 K. At the end of each test period, the mass and final pH of each flask was recorded (“Final pH” in Table 2). The method used here is similar to that described by Sunder *et al.* [24].

A 20 mL disposable syringe was used to extract approximately 20 mL of solution from the flask. Vacuum filtration was used to remove any undissolved solids from the solution. The filtration apparatus consisted of a Millipore filter paper (0.025 μm diameter pore size) and a 250 mL glass Erlenmeyer flask with sidearm. After filtration, the solution was transferred to a 20 mL glass scintillation vial. The mass and volume of the solution was determined. The solution was then preserved by adding 100 μL concentrated nitric acid using an Eppendorf auto-pipette. Vials were sealed tightly and wrapped in Parafilm to prevent losses due to evaporation.

The contents of each vial were analysed using ICP-MS and ICP-AES (Inductively Coupled Plasma-Atomic Emission Spectroscopy). ICP-MS was used to determine zirconium, yttrium and lithium concentrations. ICP-AES was used to determine some zirconium concentrations as well as silicon and sodium concentrations (from sodium silicate).

4. Results and discussion

Tests were performed in triplicate for each set of experiment conditions characterized by the solvent pH and experiment duration. Tests were carried out using solutions of three different pH values, *i.e.*, 5.75, 8.3 and 10.3. Table 2 summarizes the results of the tests completed in this study.

Table 2 Solubility tests on zirconia powder at room temperature

Test Name	Solvent pH	Initial pH	Final pH	Time (h)	[Zr] (M)	[Zr] error (M)
B.RT.10.3.1	10.3	10.26	-	73.7	6.5E-09	7E-10
B.RT.10.3.2	10.3	10.16	9.83	73.8	6.0E-09	7E-10
B.RT.10.3.3	10.3	10.28	9.94	73.9	5.9E-09	7E-10
B.RT.10.7.1	10.3	10.18	9.57	167.1	4.6E-09	4E-10
B.RT.10.7.2	10.3	10.26	9.59	167.3	8.0E-09	8E-10
B.RT.10.7.3	10.3	10.30	9.50	167.4	5.0E-09	5E-10
B.RT.10.10.1	10.39	10.16	8.70	215.1	5.6E-09	7E-10
B.RT.10.10.2	10.39	10.23	8.00	215.2	5.9E-09	7E-10
B.RT.10.10.3	10.39	10.22	9.45	215.2	1.3E-08	1E-09
B.RT.6.3.1	5.75	5.09	5.58	115.3	1.5E-09	2E-10
B.RT.6.3.2	5.75	5.16	5.29	115.5	1.5E-09	2E-10
B.RT.6.3.3	5.75	5.13	5.23	115.6	1.4E-09	2E-10
B.RT.6.7.1	5.75	5.12	5.22	163.3	1.2E-09	3E-10
B.RT.6.7.2	5.75	5.13	5.27	163.3	1.5E-09	4E-10
B.RT.6.7.3	5.75	5.12	5.23	163.3	8.8E-10	3E-10
B.RT.6.10.1	5.75	5.14	5.29	263.2	3.3E-10	-
B.RT.6.10.2	5.75	5.12	5.23	263.2	6.7E-09	8E-10
B.RT.6.10.3	5.75	4.96	5.21	263.2	4.4E-10	3E-10
B.RT.8.3.1	8.3	5.25	5.33	115.3	1.1E-09	3E-10
B.RT.8.3.2	8.3	5.25	5.37	115.2	5.5E-10	3E-10
B.RT.8.3.3	8.3	5.37	5.42	115.1	5.5E-10	3E-10

Durations of the leaching tests varied between three days to about eight days, Table 2. There were no significant differences between the results obtained from the tests carried out for three days and those carried out or eight days. This suggests that the solutions reached near equilibrium conditions after about three days. This observation is in consistent with the results reported by Ekberg *et al.* [9] who carried out tests on zirconia solubility for time periods ranging between 3 days to 6 weeks.

The solution pH dropped soon after it was added to the container containing powder ZrO_2, Table 2. A most probably explanation for this pH drop is the complexation of the OH^- ions with the zirconium ions (Zr^{4+}) as discussed earlier (Section 2.1, Equation (1)). It seems that the Zr^{4+} ions present in the solid surface are also able to complex with the OH^- ions as the drop in pH occurred in a very short time after the solution was added to the container containing the powder ZrO_2 (Section 3.2). The complexation of the OH^- ions with Zr^{4+} ions would results in a decrease in OH^- ions concentration that would result in an increase in the H^+ ion concentration and a decrease in the pH). This hypothesis is supported by similar solubility tests that we carried out with a ZrO_2 sample consisting of much smaller particles and hence of larger surface area (~25 m^2/g). In these tests a much larger drop in the solution pH was observed when the solution was added to the solid powder.

Table 2 gives the zirconium concentration in the solution at the end of each test. The error in the Zr concentration shown in this Table is the precisions in the concentration measurement for that test. It is the uncertainty in the Zr concentration determination using ICP-MS. Table 3 summarizes the results given in Table 2. It gives room temperature solubility of zirconia in the three solutions investigated in this work. The solubility shown is the average of the results shown for the respective solvent in Table 2. The uncertainty in the solubility value at a given pH shown in Table 3 is the average deviation in the Zr solubility values for the pH listed in Table 2.

Table 3 Room temperature solubility of zirconia

Solvent pH	[Zr] (M)
10.3	6.7E-9 ± 1.7E-9
8.3	7.3E-10 ± 2.4E-10
5.75	1.7E-9 ± 1.1E-9

The results obtained here for the solubility of zirconia are compared with those reported in the literature in Figure 1. It is clear from the data shown in this figure that the solubility of zirconia is lower in the pH region between 5.8 and -10.3, than its solubility in the solutions with pH values less than 5.8 or greater than 10.3. The results obtained here are important for the use of zirconia as a host matrix for using-up "excess weapon plutonium", for "burning" minor actinides, and for using burnable nuclear absorbers to control the neutron flux in nuclear reactors. The coolant pH in most of the water-cooled reactors is in the region between 7 and 10.3, the pH region investigated in this work. The low solubility of zirconia in this pH region would help reduce the release of the components from the zirconia matrix into the coolant in case of a defect in the cladding.

Also, the pH of the groundwater in the Canadian granite shield, at the planned depth of the geological disposal vault is between 6-9 [6], the pH region investigated here. Thus, the results obtained in this work support the selection of zirconia as a host matrix for the direct disposal of actinides (plutonium and MA), if desired, in a geological disposal vault.

5. Summary and conclusions

The literature on the solubility of zirconia was reviewed. The existing literature was found to indicate a large range of values for the solubility of zirconia in the pH region of interest for its nuclear applications. Only a few groups have published experimental results in the intermediate pH region and their solubility limits differ by several orders of magnitude.

The solubility values of zirconium ([Zr] (M)) in solutions of initial pH values of 5.75, 8.3 and 10.3 measured in this work are 6.7E-9 ± 1.7E-9, 7.3E-10 ± 2.4E-10, and 1.7E-9 ± 1.1E-9, respectively. Solubility values for zirconia obtained here are lower than the previously published experimental values.

The low solubility of zirconia in the pH region between 5.7 and 10.3 supports its use as an inert host matrix for actinides (Pu and MA) to "burn" them in a nuclear reactor, and for burnable neutron absorbers (such as Gd and Dy) to control the neutron flux in a nuclear reactor. Also, it supports the use of zirconia matrix as a host matrix for the direct disposal of radionuclides (which can be incorporated in its lattice such as actinides and lanthanides) in a geologic disposal vault.

6. References

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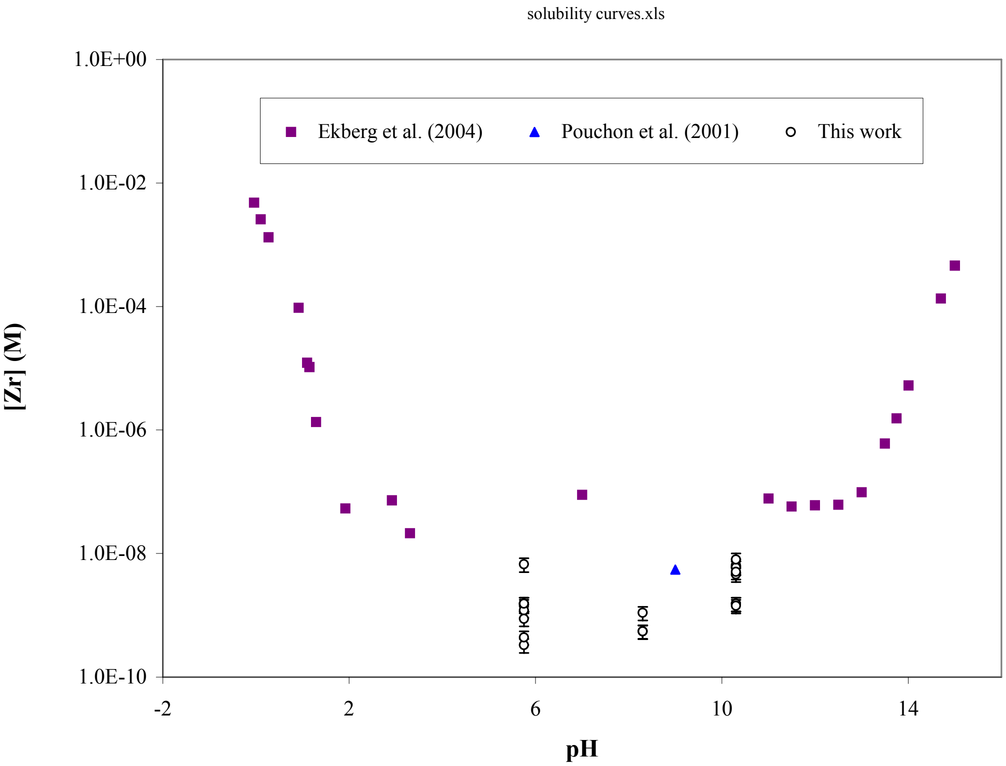

Figure 1 Zirconia solubility at room temperature as a function of solvent pH

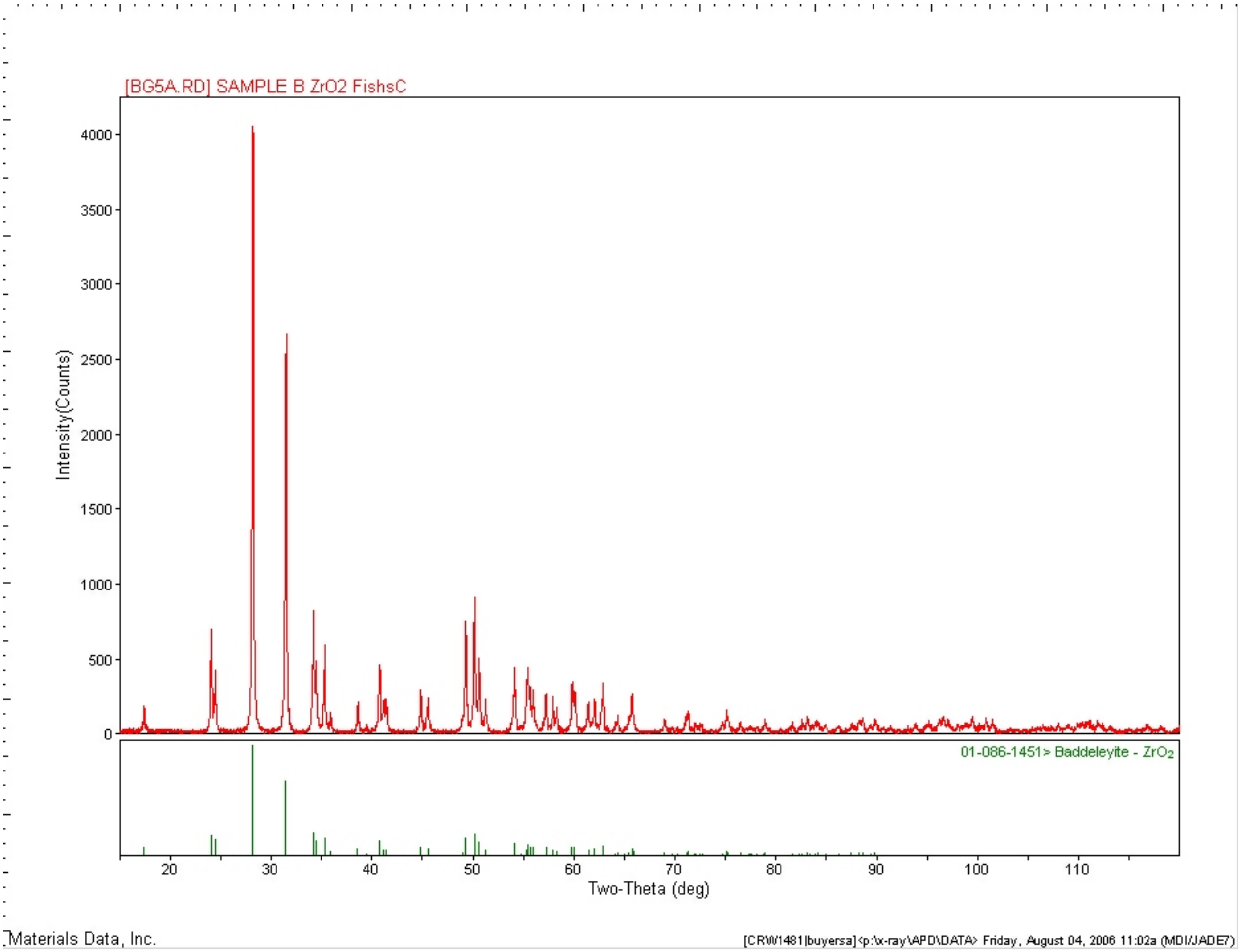

Figure 2 Comparison of X-ray diffraction spectra for zirconia sample used in the solubility tests with reference zirconium dioxide spectra [23]

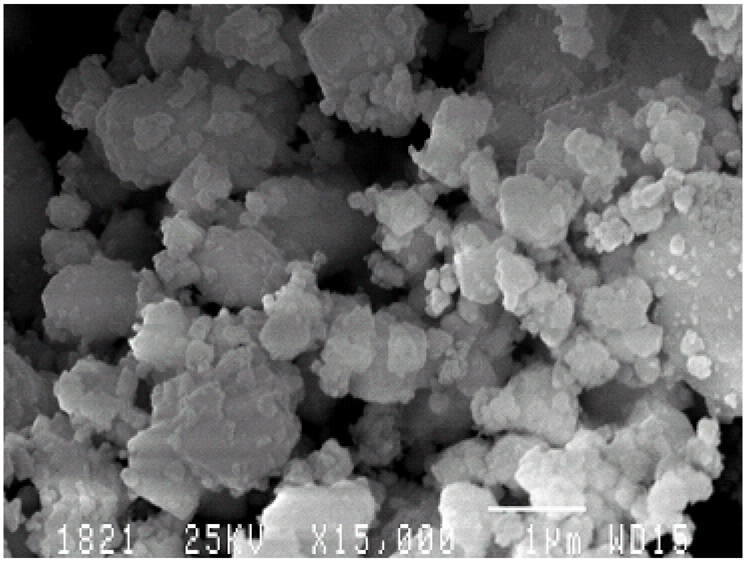

Figure 3 SEM image of zirconia used in the solubility tests at 15, 000X magnification