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Solubilities of Fission Products under Supercritical Water-cooled Reactor Conditions

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Abstract

The literature data on the solubilities of selected fission products expected to exist as oxides in sub- and supercritical water solutions are reviewed in this paper. While the solubilities of most metal oxides and inorganic salts typically decrease rapidly as the temperature becomes supercritical, the solubilities of some actinides and some fission products increase with increasing temperature or are independent of temperature. Like most metal oxides, the major dissolved species of oxide fission products are neutral species in supercritical water, which is a concern for all direct cycle SCWR concepts as these species can be easily transported to parts of the system outside of the reactor core.

1. Introduction

The proposed Canadian supercritical water-cooled reactor (SCWR) is to be designed to operate such that the coolant temperature increases from 350 to 625 °C across the core at 25 MPa. As uranium undergoes fission and produces the energy to heat the coolant, various fission products are produced, which, includes noble gases and iodine, Ag, Ba, Ce, La, Mo, Nb, Nd (and other lanthanides), Pd, Rh, Ru, Sn, Sr, Y and Zr. In the event of a defect of the fuel cladding, these fission products can be released to the coolant and transported to parts of the system outside of the reactor core, resulting in an increase in radiation fields and dose to nuclear workers [1].

Fission products such as the alkali metals and halogens are typically soluble in sub-critical water while the oxides of other fission products, such as $^{95}ZrO_2$, are barely soluble. As the temperature changes from sub-critical to supercritical in SCWR, the drastic decrease in density and dielectric constant of supercritical water (SCW) can result in a rapid decrease in the solubility of many inorganic compounds [2]. For example, NaCl has a high solubility in sub-critical water (357 g/kg H_2O at 25 °C); however, its solubility is only 0.17 g/kg H_2O at 408 °C and 22.4 MPa [3]. The effects of temperature, pressure, pH and redox conditions on the dissolution behavior of typical corrosion products have been discussed previously [2]. However, the behavior of fission products under SCWR conditions has rarely been discussed, partially due to the lack of data at high temperatures. Since the transport of fission products is important not only for activity transport modeling but also for SCWR design and fuel qualification, this paper reviews the dissolution behavior of some selected fission product oxides under SCWR chemistry conditions. As UO_2 and ThO_2 are proposed as fuels in various SCWR concepts and will be the matrix in which most fission products are formed, their solubilities are also discussed.

2. Solubilities of Nuclear Fuels UO_2 and ThO_2

2.1 UO_2

The solubility of UO_2 has been studied by many groups [4, 5] because of its importance as a nuclear fuel. However, the differences in measured solubilities of UO_2 can be as large as four orders of magnitude due to the differences in morphology of UO_2 (crystalline or amorphous), redox conditions (O_2 ingress typically increases the solubility) and equilibration time.

The solubility of uranium oxide decreases with increasing pH at pH<5 (Figure 1) because U(IV) can be present as a number of different hydrolysis species. When pH is above 5, the solubility of crystalline UO_2 is almost independent of pH as it is present almost completely as the neutral species $U(OH)_4°$. It appears that microcrystalline and amorphous UO_2 have similar solubilities at pH>5 [5, 6] although theoretical calculations showed that crystalline $UO_2(c)$ has a much lower solubility (Figure 1). The measured high solubility of $UO_2(c)$ is largely due to the hydration of crystalline UO_2 resulting in the formation of an amorphous phase on the surface of the bulk phase. On the other hand, amorphous UO_2 can also partially re-crystallize to form microcrystalline phases during the dissolution process. In neutral water, most measured values for the solubility of UO_2 range from 10^{-7} to 10^{-9} mol/kg at 25 °C, which can be assumed to be the concentration of the neutral species $U(OH)_4°$. The thermodynamically calculated solubilities of amorphous and crystalline UO_2 are 3.16×10^{-9} and 1.38×10^{-15} mol/kg, respectively, in neutral water at 25 °C [6].

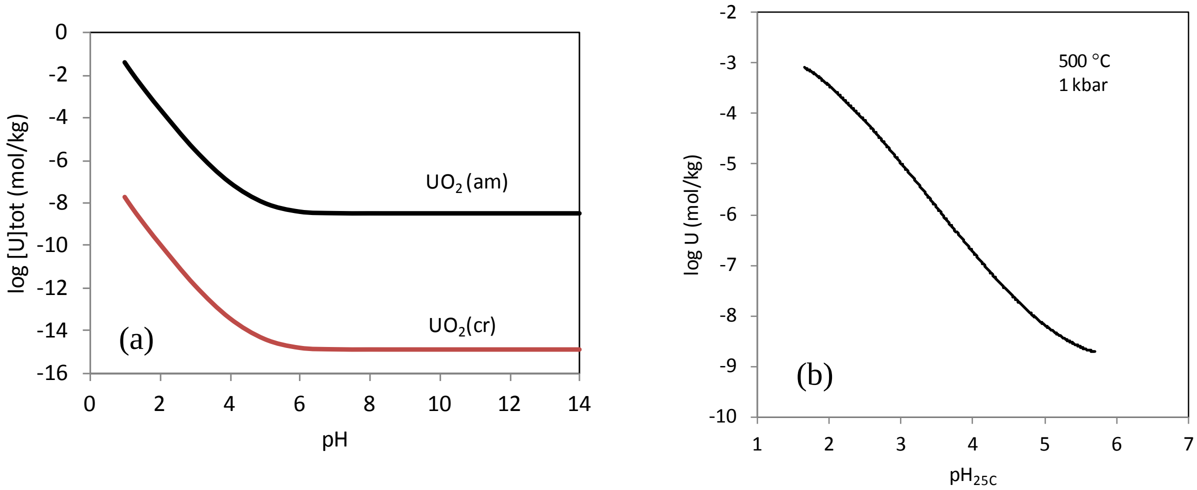

Figure 1: (a) Thermodynamically calculated solubilities of $UO_2(c)$ and $UO_2(am)$ at 25 °C as a function of pH; (b) Solubility of $UO_2(c)$ at 500 °C as a function of pH using a Ni-NiO buffer [7].

The solubility of crystalline $UO_2(c)$ at temperatures from 100 to 300 °C and pH from 1 to 10 was studied by Parks and Pohl [8] at 50 MPa in reducing aqueous solutions. In acidic solutions with pH<2 and at temperatures below 200 °C, the dominant dissolved species is $U(OH)^{3+}$. At higher pH, the only important dissolved species is $U(OH)_4°$, and $U(OH)_5^-$ does not contribute to the solubility of UO_2, showing that the solubility at pH>4 is independent of pH, similar to the results at 25 °C. Their results also showed that the temperature effect on the solubility of UO_2 at pH> 4 was insignificant, which agrees with the results of Tremaine et al. [9]. The equilibrium constant of the dissolution reaction

$$UO_2(c) + 2\,H_2O = U(OH)_4{}^{\circ} \qquad (1)$$

had the value $\log_{10}K_{sp} = -9.47\pm0.3$, and was equal to the concentration of $U(OH)_4{}^{\circ}$, 3.39×10^{-10} mol/kg. The solubility of $UO_2(c)$ in neutral water is about 10 times lower than the theoretical value of $UO_2(am)$ but about 5 orders of magnitude greater than the thermodynamically calculated solubility of crystalline UO_2, indicating that an amorphous layer of $UO_2(am)$ probably formed on the surface of bulk $UO_2(c)$.

Red'kin et al. [7, 10] studied the solubility of crystalline UO_2 under SCW conditions at temperatures from 300 to 600 °C and a pressure of 100 MPa at different pHs. Their results showed that the solubility of $UO_2(c)$ in pure water was independent of temperature and buffer (Ni/NiO or Fe_2O_3/Fe_3O_4) within experimental uncertainty and has the average value of $\log_{10}S$ (mol/kg) = -9.0 ± 0.5. Their value is similar to that reported by Parks and Pohl [8] for sub-critical conditions. In HCl solutions, the solubility of UO_2 decreases with increasing pH (Figure 1b), which appears to contradict the results of Kovalenko et al. [11], who recently measured the solubility of $UO_2(c)$ in supercritical solutions at 500 °C and 100 MPa. They reported that the solubility of UO_2 is 1×10^{-6} mol/kg, independent of HCl concentration in the range of 0.001 to 0.05 m, and this value can be accepted as the solubility in pure water. They found that $U(OH)_4{}^{\circ}$ was the major dissolved species in 0.001 to 0.05 mol/kg HCl solutions. This value is about two orders of magnitude greater than the value of Red'kin et al. [10].

2.2 ThO_2

The solubility of ThO_2 has been studied at room temperature by many groups over the past six decades [6, 12]. Like UO_2, the solubility of ThO_2 can be affected by its morphology, the pH of the test solutions, formation of colloidal particles and the experimental method. A difference in reported value of 3 to 4 orders of magnitude can be found in the open literature. In neutral and alkaline solutions where the solubility is low, the sorption of dissolved species on filter materials can lead to scatter in the measured solubility data. The solubility behaviour of $ThO_2(am)$ or $ThO_2(c)$ can be divided into two regions: below pH 6 and above pH 6 (Figure 2), discussed below.

The solubility constant of the reaction (2) for amorphous ThO_2 (am) in acidic solutions was determined around room temperature [12].

$$ThO_2(am) + 4\,H^+ = Th^{4+} + H_2O \qquad (2)$$

or

$$Th(OH)_4 = Th^{4+} + 4\,OH^- \qquad (3)$$

The average value of the solubility constants at 25 °C evaluated by various groups is $\log K_{sp} = 8.9 \pm 1.1$ for equation (2) and $\log K_{sp} = -47.1\pm1.1$ for equation (3), respectively.

The dissolution of crystalline $ThO_2(c)$ in acidic solutions is usually slow and the solubility can be measured using super-saturated solutions heated to high temperature and then cooled to precipitate ThO_2. As expected, the solubility of crystalline ThO_2 in acidic solution is lower than that of amorphous ThO_2 (Figure 2). Neck et al. [13] measured the solubility of crystalline ThO_2 using coulometric pH titrations

$$ThO_2(c) + 4H^+ = Th^{4+} + 2H_2O \qquad (4)$$

or $$ThO_2\,(c) + 2H_2O = Th^{4+} + 4\,OH^-. \quad (5)$$

Their measured solubility constant agrees with that calculated from thermodynamic functions. The value of $\log K_{sp}$ for reactions (4) and (5) are 1.77±1.11 and -54.24 ±1.11, respectively, about 7 orders of magnitude lower than that of amorphous ThO_2(am).

In neutral and alkaline solutions, the solubility of ThO_2 is independent of pH from pH 6 to pH 14. Although crystalline ThO_2(c) has a lower solubility than amorphous ThO_2(am) or $Th(OH)_4$(s) (Figure 2), the measured solubility of these two phases usually has the same value because of the formation of an amorphous layer of ThO_2 on the surface of the bulk material, which is similar to the behaviour of UO_2 dissolution. The dissolution reaction in this region can be expressed as

$$ThO_2(am) + 2\,H_2O = Th(OH)_4^{o} \quad (6)$$

The equilibrium constant of reaction (6) has a value of $\log K_{s14} = -8.5 \pm 1.0$ at 25 °C [6, 12]. The value of K_{s14} can be assumed to be the concentration of $Th(OH)_4°$, 3.16×10^{-9} mol/kg to calculate the solubility of ThO_2(am). However, the value probably also includes the concentration of neutral polynuclear species with sizes less than 2 nm [12].

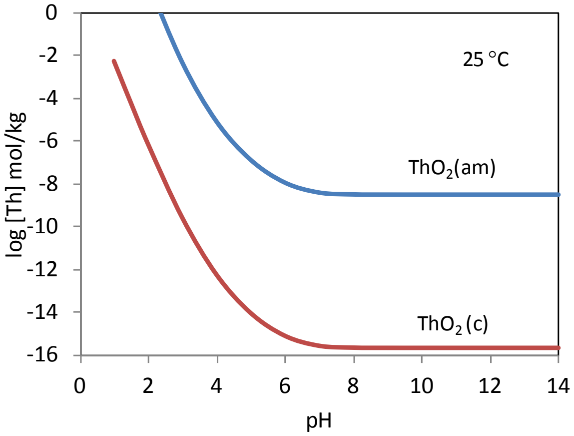

Figure 2: Thermodynamically calculated solubility of ThO_2 at 25 °C as a function of pH.

Rai et al. [14] measured the solubility of crystalline ThO_2(c) at 23 and 90 °C in HCl and their value for the solubility constant was $\log K_{sp} = 1.76 \pm 0.2$ for equation (4) and -51.4±0.2 for equation (5) and at 90 °C. Although their results showed that the solubility of ThO_2 increased with increasing temperatures, the value of $\log K_{sp}$ at 90 °C for equation (4) is actually same as that at 25 °C [13], indicating that temperature does not have a significant effect on the solubility product of ThO_2. It is not known how temperature affects the solubility of ThO_2 in near neutral or alkaline solutions at higher temperatures, especially under SCWR conditions. Considering the similar dissolution behaviours of UO_2 and ThO_2 and their similar solubility values at room temperature, it is possible that the solubility of ThO_2(c) is less dependent on temperature in neutral and alkaline solutions and the value in SCW may be close to that of UO_2.

3. Solubility of Selected Fission Products

As discussed above, solubility of fission products in SCW are rarely reported. Nevertheless, the dissolution behaviours of oxides of some fission products in SCW were investigated in recent years and were discussed in this section. The systems [$Sr(OH)_2 + H_2O$] and [$SrCl_2 + H_2O$] also were chosen because of their importance to modeling fission product transport in SCWR reactors, and because they are soluble in near-critical water and so may be used as model systems for other M^{2+} species.

3.1 Sb_2O_3

Crystalline antimony (III) oxide (Sb_2O_3) has two phases: valentinite and senarmontite. Although valentinite (orthorhombic phase, $\Delta G_f^{\circ}(298K) = -625.93$ kJ/mol) is more commonly found in nature than senarmontite (cubic, $\Delta G_f^{\circ}(298K) = -633.46$ kJ/mol) [15], senarmontite is thermodynamically more stable at room temperature. The solubilities of valentinite and senarmontite increase with increasing temperature in pure water and have the values of 6.214×10^{-5} and 1.046×10^{-5} mol/kgH_2O at 25 °C, respectively (Figure 3a).

Unlike many metal oxides and inorganic salts, whose solubilities decrease rapidly near the critical point of water [2], the solubility of Sb_2O_3 increases with increasing temperature in SCW at pressures of 500 bar [15] and 600 bar [16] (Figure 3b). The presence of chloride increases the solubility of Sb_2O_3 in solution because of the formation of chloride complexes.

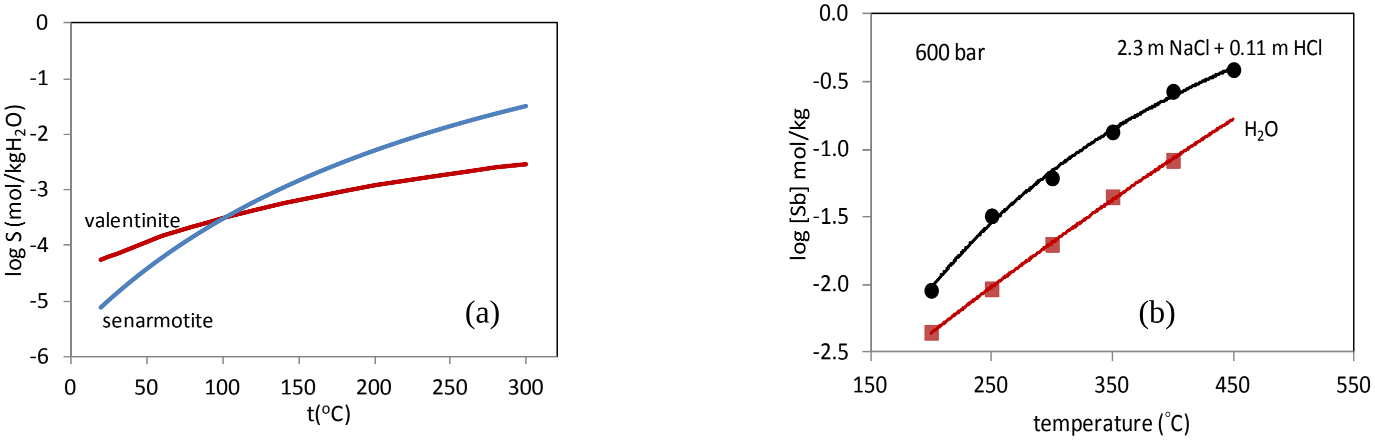

Figure 3: (a) Solubilities of valentinite and senarmontite in pure water [15]; (b) Solubilities of senarmontite in pure water and chloride solutions [16].

The solubility of Sb_2O_3 is independent of pH between pH 2 and 11 (Figure 4) because the major dissolved species in this pH region is the neutral species, $Sb(OH)_3^{\circ}$ from room temperature into the supercritical region [15, 16].

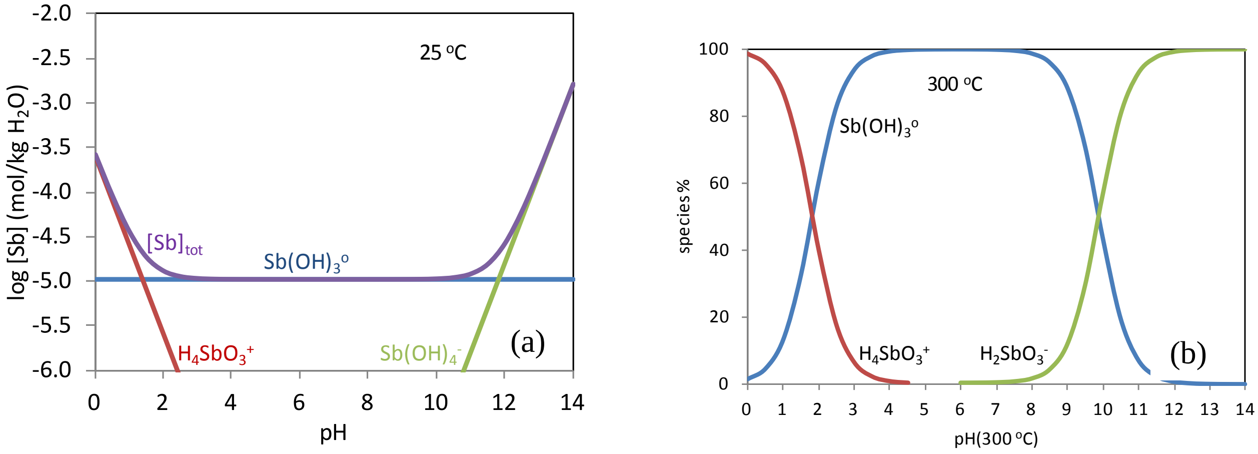

Figure 4: (a) Solubility of senarmontite and concentration of dissolved Sb(III) species as a function of pH at 25 °C; (b) distribution diagrams for dissolved Sb(III) species at 300 °C.

3.2 $Sr(OH)_2$ and $SrCl_2$

Zimmerman et al. [17] recently reported preliminary results of an experimental study to determine the association constants of strontium with hydroxide and chloride ions at temperatures up to 350 °C, using high-pressure flow AC conductance. Under SCWR conditions the formation of $SrOH^+$ and $Sr(OH)_2^0$ ion-pairs was established to be greater than $SrCl^+$ and $SrCl_2^0$ ion pairs, so that hydroxy complexes will be the dominant strontium species in solution. Neutral species were found to be substantial at 350 °C at concentrations above 10^{-3} mol kg^{-1}, for both salts. These data are an important first step in determining whether the neutral $Sr(OH)_2^0$ may be sufficiently soluble in SCW to be carried to the high pressure turbines.

3.3 MoO_3

The solubility of MoO_3(c) in subcritical water increases with increasing temperature (Figure 5) below 300 °C and has a value of 1.39×10^{-2} mol/kg at 300 °C [18]. The solubility of MoO_3 in water vapour was measured to be between 10 and 300 $\times10^{-6}$ mol/kg at temperatures from 300 to 360 °C and pressures from 40 to 150 bar [19].

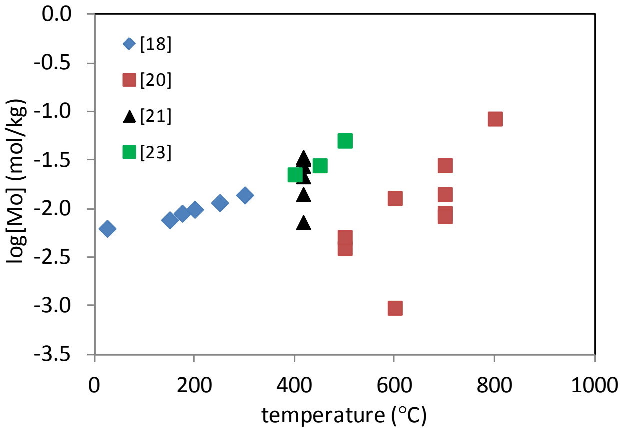

Figure 5: Solubility of MoO_3 in subcritical and supercritical water.

The solubility of MoO_3 in supercritical water was reported by Ulrich and Marvrogenes [20] from 500 to 800 °C and 200 MPa, Gong et al. [21] at 417 °C and 29 to 150 MPa, Glemser et al. [22] at temperatures from 400 to 600 °C and pressures from 32 MPa to 180 MPa, and Meredith et al. [23] at temperature from 400 to 500 °C and pressure from 44 to 113 MPa. The solubility did not change significantly with increasing temperature and pressure from the subcritical to supercritical region considering the large experimental uncertainty (more than 1 order of magnitude from different or even the same authors at the same temperature and pressure) (Figure 5). More reliable experimental methods are required to accurately determine the solubility of MoO_3 in aqueous solutions.

The speciation of dissolved Mo(VI) was studied by Minubayeva and Seward [24]. Below 150 °C, the major dissolved species are $H_2MoO_4°$, HMO_4^- and MoO_4^{2-}; as the temperature increases to 250 °C, the major dissolved species are $HMoO_4^-$ and MoO_4^{2-} (Figure 6). In pure SCW, $H_2MoO_4°$ is the only important species in neutral solutions [20]. Recently, Yan et al. [25] studied Mo^{6+} speciation using *in situ* X-ray spectroscopy and concluded that MoO_4^{2-} is a dominant species in neutral water between 400 and 600 °C at density of 0.5 to 0.6 g/cm^3 although the presence of $HMoO_4^-$ and $H_2MoO_4^o$ cannot be completely discounted.

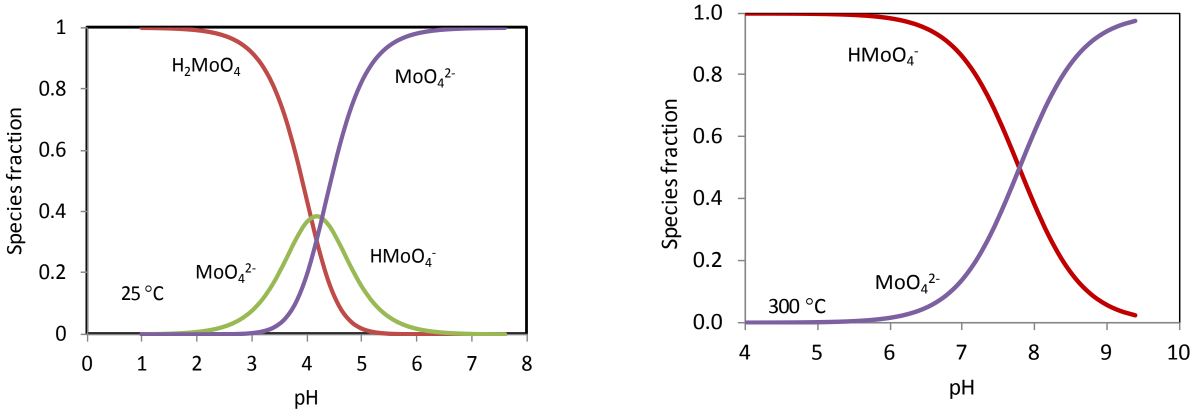

Figure 6: Calculated Mo (VI) speciation in subcritical aqueous solutions at 25 and 300 °C using dissociation equilibrium constants of H_2Mo_4 [24].

3.4 ZrO_2

The solubility of amorphous and crystalline phases of ZrO_2 at room temperatures was summarized in reference [2]. The only solubility data for crystalline ZrO_2 from 25 to 300 °C at pH 10 and saturation pressure was measured by Qiu et al. [26]. Their results showed that the average value of solubility is 5.5×10^{-8} mol/kg at 25 °C and is the same as that for $Zr(OH)_4$, indicating that ZrO_2(cr) dissolves through the formation of $Zr(OH)_4$ on the surface of ZrO_2(c). The solubility of ZrO_2(c) decreases to 0.91×10^{-8} mol/kg at 250 °C and then the solubility increases with increasing temperature (Figure 7).

The solubility of ZrO_2(c) in alkaline and acidic supercritical solutions was studied by Korzhinskaya [27] and Ryzhenko et al. [28]. Their results show that the solubility of ZrO_2 in weakly acidic and alkaline solutions is 1.28×10^{-5} mol/kg at 400 °C and 100 MPa and is independent of pH. The value is two orders of magnitude greater than that measured at 300 °C and 10 MPa; as temperature increases, the solubility of ZrO_2 decreases to 3.72×10^{-6} mol/kg at 500 °C and then increases to 8.9×10^{-6} mol/kg at 600 °C and 100 MPa [28].

The speciation of dissolved ZrO_2 has been studied at 25 °C and $Zr(OH)_4°$ is the major species between pH 2 and pH 13 [26]. The dissolution behaviour and the dominant dissolved species as a function pH at elevated temperature are similar to those at room temperature. Data in SCW solutions showed that $Zr(OH)_4°$ is the dominant species in weakly acidic and alkaline solutions as the solubility of ZrO_2 is independent of pH (Figure 7b) [27, 28].

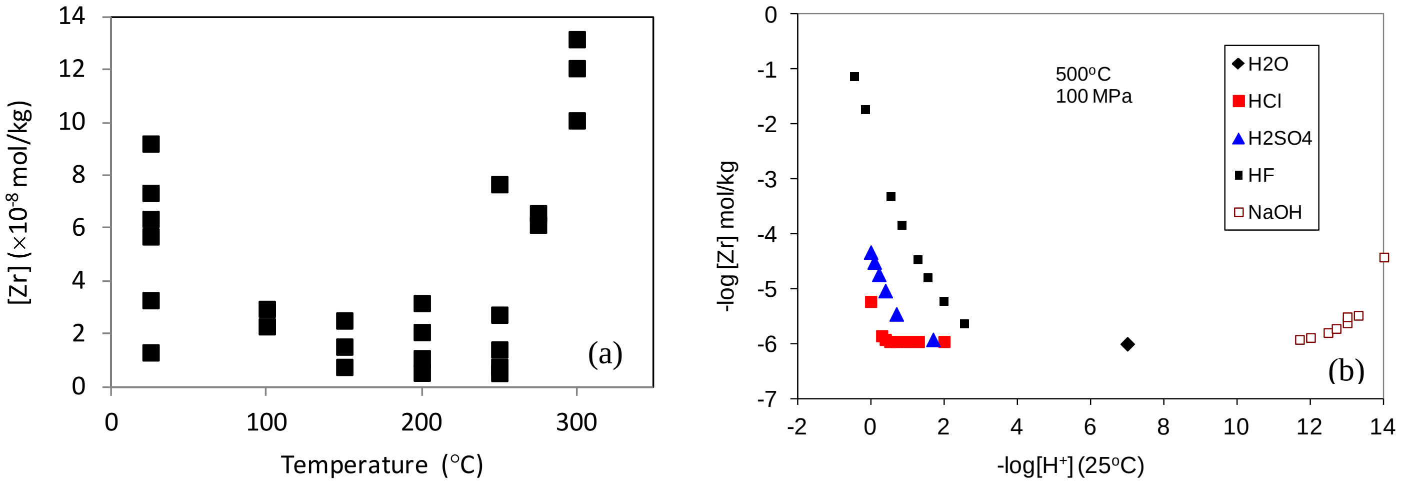

Figure 7: Solubility of ZrO_2 as a function of (a) temperature at pH 10 [26]; (b) $[H^+]$ at 500 °C and 100 MPa [28].

4. Conclusions

The solubilities of nuclear fuels and some selected fission product oxides in subcritical and supercritical water solutions were reviewed. The solubilities of these compounds did not show a maximum as typical oxides or inorganic salts such as (CuO and NaCl) near supercritical region. The solubility of UO_2 and probably ThO_2 do not change as the temperature increases from the subcritical to the supercritical region while the solubility of Sb_2O_3 increases with increasing temperature. The solubility of ZrO_2 in neutral SCW (600 °C, 100 MPa) is about 2 orders of magnitude greater than that under subcritical conditions (300 °C, 10 MPa). The increase of temperature from subcritical to supercritical region does not significantly increases the solubility of MoO_3.

Similar to the dissolution of most metal oxides, the major dissolved species of UO_2, ThO_2, Sb_2O_3 and ZrO_2 around pH 7 in SCW are the neutral species, $U(OH)_4°$, $Th(OH)_4°$, $Sb(OH)_3°$ and $Zr(OH)_4°$, respectively; for MoO_3, both $H_2MoO_4°$ and MoO_4^{2-} are found to be dominant species by different groups. The major dissolved species of $SrCl_2$ and $Sr(OH)_2$ in SCW are expected to be $Sr(OH)_2°$ and $Sr(OH)^+$.

Some fission products (Sb, Mo) are quite soluble in SCW and their radioactive neutral species can be transported to the turbine and downstream piping as dissolved species, resulting in increased dose exposure to nuclear workers.

Data on the solubility of many fission products under SCWR chemistry conditions are not available, and experimental measurements of these data are required in order to develop predictive model of activity transport.

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