AN OVERVIEW OF CORROSION PRODUCTS SOLUBILITIES IN SUBCRITICAL AND SUPERCRITICAL WATER

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Abstract

Solubility is a fundamental property of materials which influences both the dissolution of oxide films on alloys and the deposition rate of resulting corrosion products. In a supercritical water reactor (SCWR), the decrease in water density from subcritical to supercritical regions can result in a decrease of solubility and deposition of corrosion products. Such deposition in the reactor core can seriously affect the fuel performance, thermalhydraulics and activity transport in an SCWR. This paper reviews the solubilities of some potential corrosion products in subcritical and supercritical aqueous solutions. The effects of temperature, pressure and water chemistry on the solubilities of corrosion products are discussed.

1. Introduction

The conceptual supercritical water-cooled nuclear reactors (SCWRs) will operate between 300 and 625°C at 25 MPa. These reactors have many advantages over existing water-cooled reactors, such as higher thermal efficiency and much simpler design, and are expected to produce power within the next two decades. The significant changes in physical and chemical properties of water as the temperature increases from the subcritical region to supercritical region result in many challenges for the SCWR design [1], including selection of alloys with adequate corrosion resistance, and the choice of water chemistry and chemistry control strategies to minimize corrosion, and corrosion product and activity transport. Solubility is a key parameter influencing both the dissolution and deposition of corrosion products. As the temperature changes from subcritical to supercritical conditions, the drastic decrease of density of supercritical water (SCW) can result in a rapid decrease in the solubility of corrosion products; the resultant heavy deposition of metal oxides in the reactor core can seriously affect fuel performance, thermalhydraulics and activity transport [2]. For example, heavy deposition of copper oxides was observed in the high pressure turbine of early fossil SCW plants in the USA, which resulted in the disassembly of the units in the first year of operation [3]. In supercritical water oxidation (SCWO) processes, precipitation of inorganic salts such as NaCl and Na_2CO_3 due to their low solubility in SCW resulted in rapid plugging of reactors or associated piping [4]. The deposited salts accelerated the corrosion rate of components in SCWO facilities and eventually lead to the shutdown or failure of expensive process equipment. This paper reviews the data on the solubility of some metal oxides relevant to the development of SCWR, and discusses the effects of temperature, pressure and water chemistry on the solubility of these metal oxides.

2. Influence of the physical and chemical properties of supercritical water on the solubility

As temperature increases, the thermal motion of water molecules destroys the hydrogen-bonded structure, resulting in a decrease in density (Figure 1) and static dielectric constant (Figure 2) [5,6]. At 30 MPa, the dielectric constant of water drops monotonically from a value of 80 at ambient temperature down to about 10 at the critical temperature (a value similar to octanol at ambient conditions) and then down to about 2 at 425°C (a value similar to cyclohexane at ambient conditions).

The low dielectric constant makes supercritical water behave like a nonpolar solvent, so that many organic compounds that are barely soluble under subcritical conditions are miscible with SCW, while compounds that are soluble under subcritical conditions will be immiscible with SCW (Figure 3) [7]. The reduced dielectric constant means that in SCW solutions there are not sufficient ion-dipole interaction energy and hydration energy between water molecules and ionic compounds to overcome ion-ion interactions of ionic compounds, and the dissolved species of many electrolytes such as NaCl, NaOH and HCl exist mainly as ion pairs [8,9].

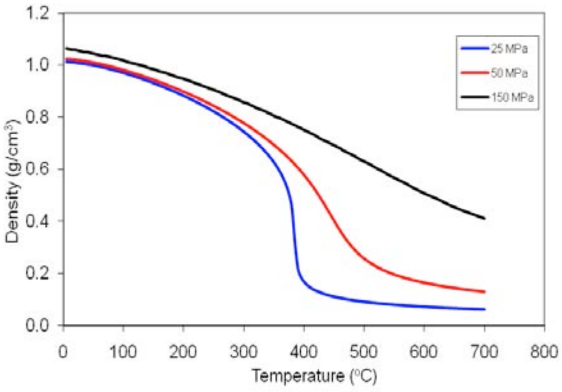


Figure 1. Density of water as a function of temperature and pressure [5].

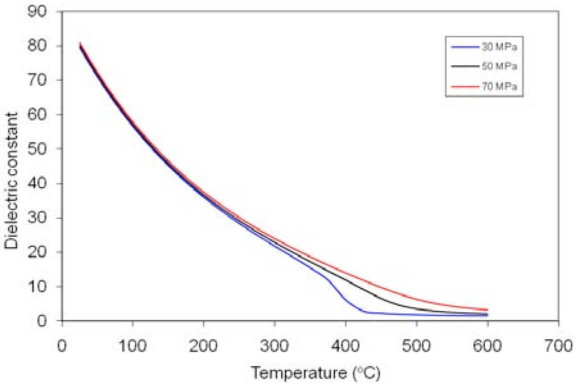


Figure 2. Dielectric constant of water as a function of temperature and pressure [6].

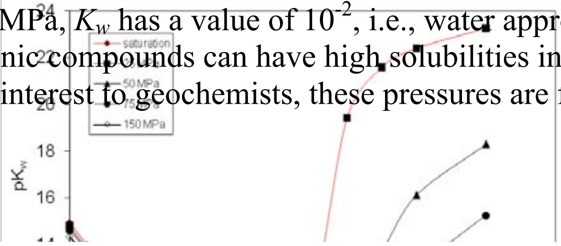
The reduced density of SCW also significantly changes the ionic product of water (K_w), which is a function of temperature and density [10]:

$$\log_{10} K_w = -4.098 - \frac{3245.2}{T} + \frac{2.2363\times10^5}{T^2} - \frac{3.984\times10^7}{T^3} + \left(13.957 - \frac{1262.3}{T} + \frac{8.5641\times10^5}{T^2}\right)\log_{10}\rho \quad (1)$$

where T is the temperature (in kelvin) and ρ is the density of water (in g/cm^3). The value of K_w as a function of temperature and pressure is shown in Figure 4.

Consider a SCWR operating at temperatures between 300°C to 625°C and a pressure of 25 MPa. Between 300°C and 350°C, the pK_w increases by only 0.6 units, but as the temperature increases from 350 to 400°C, the value of pK_w increases by 7.3 units due to the drastic decrease of water density over this temperature range. A further temperature increase from 400 to 625°C leads to a pK_w increase by 4 units (Figure 4). The significant increase of pK_w (decrease of K_w) indicates that water under SCWR conditions will be only slightly dissociated. For example, the pH of neutral water increases from 5.6 at 300°C to 11.7 at 625°C and 25 MPa (Figure 5). Note for neutral water pH=1/2 pK_w. As K_w, and hence the concentrations of H^+ and OH^-, decreases, the dissolved species of many metal oxides in SCW form hydration compounds (e.g., $M_xO_y{\cdot}nH_2O$) or neutral species.

It should be noted that a large ionic product of water can be obtained at high pressures; Equation 1 shows that at constant temperature, the value of K_w increases with increasing density or pressure. At a temperature of 1250°C and a pressure of 20,000 MPa, K_w has a value of 10^{-2}, i.e., water approaches the behaviour of a strong electrolyte [11]. Hence, ionic compounds can have high solubilities in high pressure supercritical water. However, while of interest to geochemists, these pressures are far higher than those relevant to an SCWR.



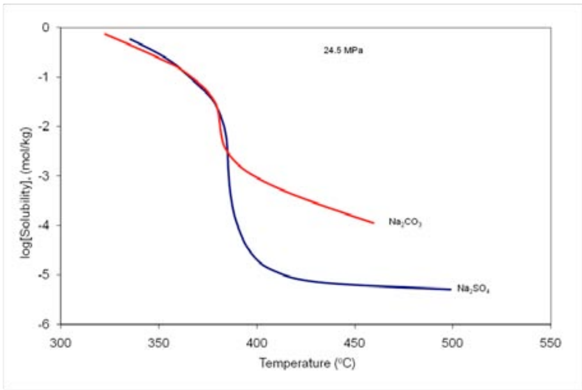


Figure 3. Solubility of Na_2CO_3 and Na_2SO_4[7].

Figure 4. Ionic product of water [10].

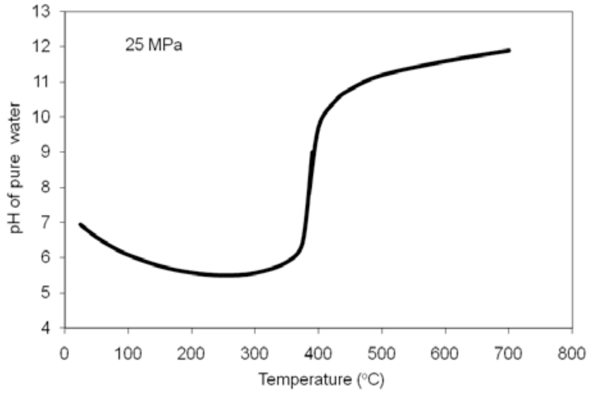


Figure 5. Calculated pH of pure water as a function of temperature at 25 MPa.

Assuming the dissolved species do not dissociate into ionic species, the dissolution of a substance in supercritical aqueous solution can be expressed as

$$M_aX_b(s) + nH_2O(l) = M_aX_b \cdot nH_2O(l), \tag{2}$$

where $M_aX_b(s)$ is an ionic compound or metal oxide; *s* and *l* refer to solid phase and liquid, respectively, and *n* is the hydration number of compound M_aX_b in supercritical aqueous solutions. The equilibrium constant, K_s, can be expressed as

$$K_s = \frac{[M_aX_b \cdot nH_2O]}{[M_aX_b][H_2O]^n}, \tag{3}$$

where the items in the brackets refer to activities of the species on a molal (mol/kg) basis. Since the solubilities of many ionic compounds and metal oxides are very low, the activity of the dissolved species can be represented as a concentration; for a pure solid phase, the activity of M_aX_b can be regarded as unity. If the activity of water is represented by the molarity (moles per liter) using the density of water, the concentration of dissolved M_aX_b can be written as

$$[M_aX_b \cdot nH_2O] = 55.56^n K_s \rho^n_{H_2O} \tag{4}$$

Using $\Delta G = \Delta H - T\Delta S$ (5)

$$\Delta H = \int \Delta C_p dT \tag{6}$$

$$\Delta S = \int \frac{\Delta C_p}{T} dT \tag{7}$$

and assuming that the difference of heat capacities ΔC_p between reactants and products of equation (2) is constant, the integration of equation (5) gives

$$\Delta G = a + bT + cT \ln T \tag{8}$$

where a, b, and c are constants.

Since
$$\Delta G = -RT \ln K_s \tag{9}$$

the combination of equations (8) and (9) leads to the expression

$$\ln S_{M_a X_b} = A + \frac{B}{T} + C \ln T + D \ln \rho \tag{10}$$

where $S_{M_a X_b}$ refers to the solubility of M_aX_b and is equal to the concentration of $M_aX_b \cdot nH_2O$ in solution; A, B and C are constants related to the entropy change and enthalpy change, and D is a constant related to the hydration number, which can be obtained using measured experimental data to fit equation (10). Hence, the solubility is a function of the temperature and density of SCW.

If the difference of heat capacity between reactants and products is zero, equation (10) can be simplified as follows:

$$\ln S_{M_a X_b} = A + \frac{B}{T} + D \ln \rho \,. \tag{11}$$

In general the solubility of most ionic compounds and metal oxides can be presented well using equations (10) and (11). Other methods, such as the use of Flory-Huggins theory to describe the dissolution behaviour of ionic compounds and metal oxides in supercritical fluid, are discussed by Leusbrock et al. [12].

Although the dependence of the solubility on pressure is generally very weak in the subcritical region, the effect of pressure on the solubility of corrosion products can be significant in SCW. Based on equations (10) and (11),

$$\left(\frac{\partial \ln S_{M_a X_b}}{\partial P} \right)_T = D \left(\frac{\partial \ln \rho}{\partial P} \right)_T \tag{12}$$

the isothermal change in the logarithm of the solubility with pressure is proportional to the compressibility of water. In general, the hydration number D and the compressibility of water are positive, hence, the solubility of oxides usually increases with increasing pressure.

3. Solubility of corrosion products in subcritical and supercritical aqueous solutions

The major alloys proposed for use in an SCWR are composed of iron, nickel, chromium, with smaller amounts of elements such as molybdenum, tungsten, vanadium, yttrium and others added to impart desired mechanical or corrosion resistance properties. Little data on the solubilities of the oxides of many of these elements in SCW have been reported. In the sections that follow, the effects of the key parameters temperature, pressure, pH and redox conditions on the solubility of various metal oxides are summarized to highlight the expected behaviors and suggest areas where further work is needed.

3.1 Temperature effect on the solubility of corrosion products

The solubilities of many metal oxides, such as CuO [13,14], PbO [13], Al_2O_3 [15], and ZnO [16], increase with increasing temperature and reach a maximum near the critical point (e.g., Figure 6). In the subcritical region, density changes are relatively small and temperature is the dominant factor affecting solubility. As the temperature approaches the critical temperature, a narrow temperature increment can reduce the water density rapidly and hence drastically change the solubility of oxides and ionic compounds. In the supercritical region, the solubilities of metal oxides change very slowly with temperature and density. As discussed above, water behaves like a non-polar organic solvent in this region, and ionic compounds and metal oxides typically have low solubilities.

Magnetite is one of the major corrosion products resulting from the corrosion of the (mainly ferrous) alloys used in nuclear reactors, and the issues arising from possible deposition of magnetite in an SCWR have been highlighted in References [1,2,17-19]. The solubility of magnetite in subcritical aqueous solution has been extensively investigated [20-24]. These data generally are agreeable within experimental uncertainty. Figure 7 shows some data on the solubility of magnetite measured as a function of temperature in pure water. Martynova [25] reported the solubility of magnetite in SCW at a pressure of 25 MPa (Figure 7). Unfortunately, Martynova's paper did not report how the data were obtained. Her study showed that the solubility of magnetite decreases rapidly with increasing temperature near the critical point and gently decreases beyond the critical point. Such deposition behavior in SCW was also observed in boiler tubes removed from the Philo plant [26], and in data from Russian fossil-fired SCW plants (as summarized in [17]). In the supercritical region, the solubility of magnetite is around 6.2 μg/kg at 25 MPa and 500^{o}C which is similar to that in CANDU coolant under normal operations [27]. Martynova's results agree with those of Holster and Schneer [28] whose measured solubility of magnetite in pure water was below their detection limit of 20 μg/kg at 400^{o}C~500^{o}C and 48.5 MPa. Figure 7 also shows the solubility of magnetite in steam as function of temperature in the superheat region [29]. The solubility of magnetite in the supercritical region estimated from Styrikovich [29], 2.1 μg/kg, agrees well with the value of 5.4 μg/kg at 25 MPa and 550^{o}C [25]. Recent theoretical calculations [17] using measured subcritical solubility of magnetite [21] also showed that the solubility of magnetite decreased sharply around 400^{o}C and 30 MPa in $2\text{-}5\times10^{-5}$ mol/kg LiOH solution.

In contrast to the behavior of the metal oxides discussed above, the solubility of WO_3 in 4 m NaCl solution continuously increases with increasing temperature from subcritical to supercritical regions (Figure 8) but the pH of solution was not reported [30]. A dissolution study of WO_3 in HCl solution [31] also show that solubility of WO_3 increases with increasing temperature between 300 and 600^{o}C at 100 MPa and follows an Arrhenius behaviour. It is not well understood why the dissolution behaviour of WO_3 is different from that of other metal oxides, although sheelite ($CaWO_4$) [32] does show a maximum in solubility over a narrow temperature region. The absence of a maximum solubility of WO_3 near the critical point appears unrelated to the presence of chloride in the tests as no tungsten-chloride complexes have been found in SCW solutions [30, 31]. It should be noted that WO_3 has a high solubility in SCW; at 500°C and 34 MPa, for example, the solubility is 31.2×10^{-3} mol/kg, which is 3×10^{4} times that of magnetite under similar conditions. Hence, tungsten should be avoided in the alloys of SCWR component to reduce corrosion and activity transport.

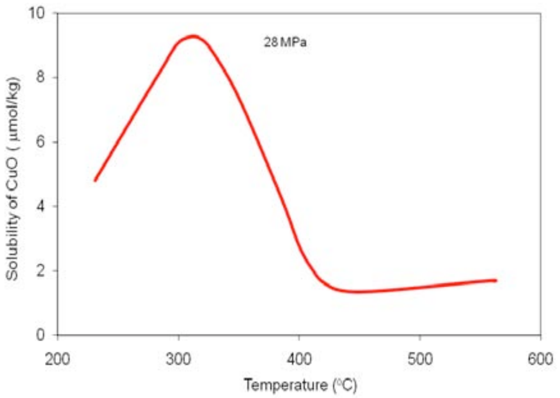


Figure 6. Solubility of CuO in pure water [14].

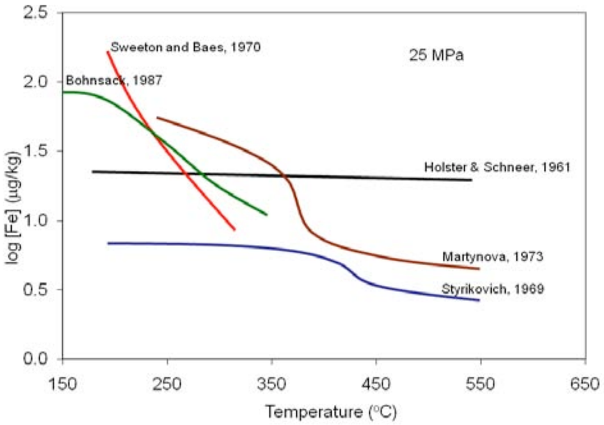


Figure 7. Solubility of magnetite in pure water.

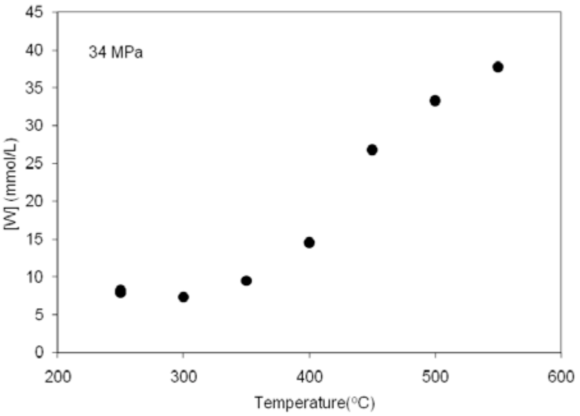


Figure 8. Solubility of WO_3 in 4 m NaCl solution at 34 MPa [30].

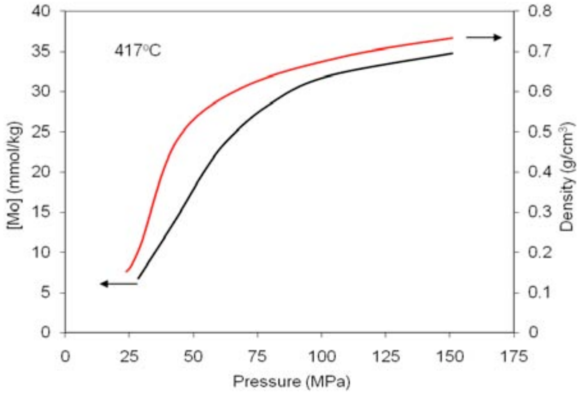


Figure 9. Solubility of MoO_3 in pure water as a function of pressure at 417°C [33].

3.2 Pressure effect on the solubility of corrosion products

The solubility of most oxides at constant temperature generally increases with increasing pressure or increasing density of water as predicted by Equation 12. Figure 9 shows the solubility of MoO_3 in pure water as a function of pressure [33]; molybdenum is commonly used in alloys to increase the material's yield strength and stress corrosion cracking resistance. Guzonas et al. [34] have reported high Mo release by corrosion of Alloy 625 and Hastelloy C in SCW. The high solubility of MoO_3 in SCW suggests that the use of alloys containing high concentrations of Mo should be avoided to minimize corrosion product and activity transport in SCWR components.

It should be noted that not all compounds show the expected pressure dependence; a decrease in solubility with increasing pressure at constant temperature was observed for minerals such as scheelite and some sulphides [35].

3.3 The effect of pH on the solubility

The discussions of solubility in the previous sections mainly focused on pure SCW. The solubility of metal oxides and the concentration of the dissolved species in SCW can also vary with pH. As an example, Figure 10 shows the solubility of ZrO_2 as a function of pH at 500°C and 100 MPa [36].

In the pH range between 3 and 12, the major dissolved species is $Zr(OH)_4^o$ which is independent of pH, and the solubility of ZrO_2 show a minimum:

$$ZrO_2(s) + H_2O\ (l) = Zr(OH)_4^o(aq) \tag{13}$$

In more acidic and alkaline solutions, the solubility of ZrO_2 increases with increasing concentration of acid or base. The dissolution behaviour of ZrO_2 as a function of pH in supercritical aqueous solution is similar to that at room temperature (Figure 11) [37-42]. Other metal oxides such as ZnO [16, 44] and TiO_2 [44,45] also show similar behaviour and form neutral species in weak acidic or weak alkaline solutions.

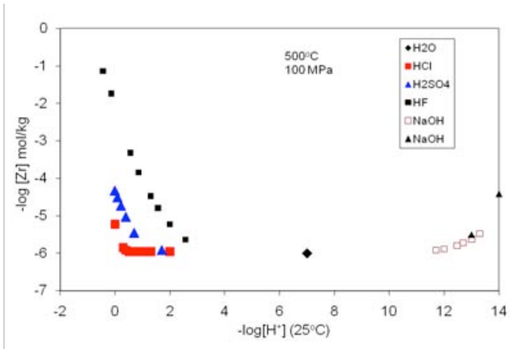


Figure 10. ZrO_2 solubility at 500°C [36].

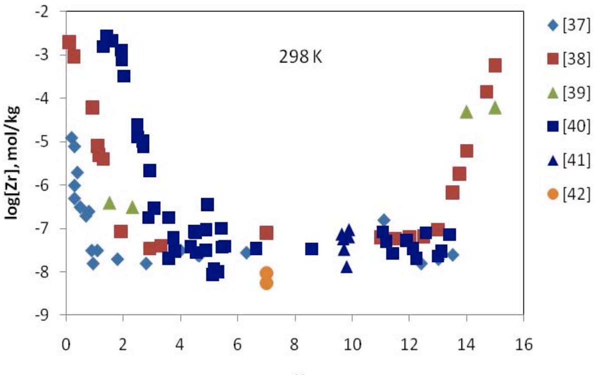


Figure 11. ZrO_2 solubility at 25°C.

Wood [31] and Wood and Vlassopoulos [46] studied the solubility of WO_3 in HCl and NaOH solution from the subcritical to the supercritical region. They found that the solubility of WO_3 is independent of HCl concentration higher than 10^{-3} M, and increases with decreasing HCl concentration, indicating that the dominant tungsten species in concentrated HCl solutions is $H_2WO_4^o$:

$$WO_3(s) + H_2O\ (l) = H_2WO_4^o\ (aq) \tag{14}$$

As the HCl concentration decreases, the anion HWO_4^- is the major dissolved species of WO_3:

$$WO_3(s) + H_2O = HWO_4^- + H^+ \tag{15}$$

In NaOH and NaCl solutions, the neutral species $NaHWO_4^o$ is the dominant dissolved species [46]:

$$WO_3(s) + NaOH^o(aq) = NaHWO_4^o(aq) \tag{16}$$

$$WO_3(s) + NaCl^o(aq) + H_2O = NaHWO_4^o(aq) + HCl^o(aq) \tag{17}$$

The solubility of WO_3 increases with increasing concentration of NaOH or NaCl.

3.4 Effect of oxidizing and reducing media on solubility

Oxidizing and reducing media can play an important role in the dissolution of oxides as observed in the solubility measurement of uranium (IV) oxide [47]. Kudrin [48] studied the effect of O_2 fugacity on the solubility of MoO_2 (Figure 12). Their results showed that the dissolved Mo(VI) concentration increases linearly with the logarithm of oxygen fugacity (f_{O_2}), indicating that Mo(VI) is the dominant dissolved species of MoO_2 under oxidizing:

$$MoO_2(s) + H_2O + 0.5O_2 = H_2MoO_4^o(sol). \tag{18}$$

Zotov et al. [49] investigated the solubility of metallic antimony in water as a function of hydrogen fugacity at 450°C and pressures of 50 and 100 MPa. They found that Sb solubility decreases linearly with increasing logarithm of hydrogen fugacity (f_{H_2}) (Figure 13). The dependence of the solubility of metallic antimony on hydrogen fugacity is consistent with the formation of $Sb(OH)_3^o(aq)$:

$$Sb(s) + 3\ H_2O = Sb(OH)_3^o(aq) + 1.5H_2 \tag{19}$$

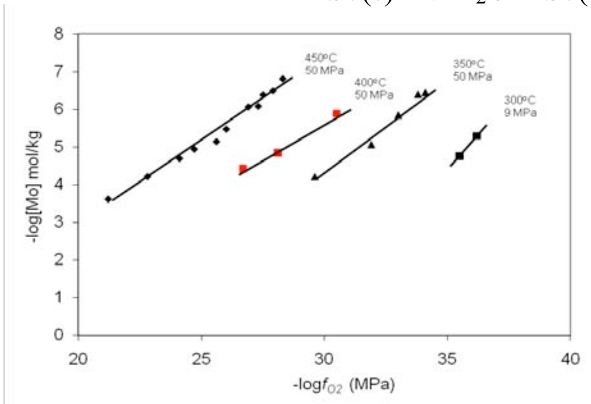


Figure 12. Solubility of MoO_2 in pure water as a function of oxygen fugacity.

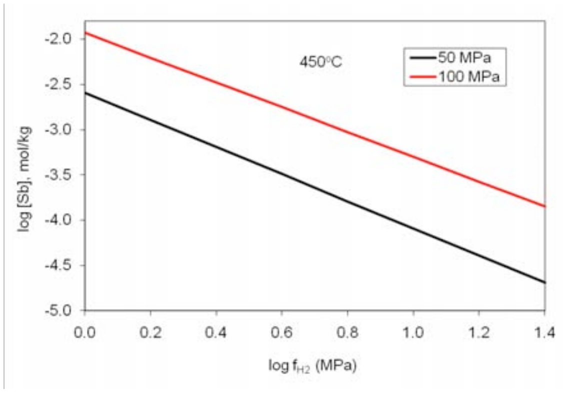


Figure 13. Solubility of metal Sb as a function of H_2 fugacity (bar) at 450°C.

The equilibrium constant of equation (19) can be expressed as

$$K_{Sb(OH)_3^0} = a_{Sb(OH)_3^0} \times f_{H_2}^{1.5} \qquad \text{or} \tag{20}$$

$$\log a_{Sb(OH)_3^0} = \log K_{Sb(OH)_3^0} + 1.5 \log f_{H_2} \tag{21}$$

The slopes of log[Sb] vs. $\log f_{H_2}$ in Figure 13 are –1.5±0.35 and –1.37±0.35 at 50 and 100 MPa respectively, which agree with slope of equation (21). The logarithm of equilibrium constants of equation (20) is –1.09±0.12 and –0.56±0.14 at 50 and 100 MPa, respectively, which increases with increasing pressure as predicted by equation (12).

4. Summary

The solubility of many oxides has been studied in supercritical aqueous solution. Some general conclusions are as follows:

- Temperature is one of most important factors affecting the solubility of metal oxides in subcritical and supercritical aqueous solutions. The solubility of metal oxides can increase or decrease with increasing temperature in the subcritical region, depending on pH and temperature range. As temperature approaches the critical point, the solubilities of metal oxide generally decrease drastically; in the supercritical region, they are less dependent on temperature.
- Density or pressure can have a significant effect on the solubility of metal oxides in supercritical water, usually increasing their solubility. However, the pressure effect is not of particular importance in an SCWR since the operating pressure in the supercritical region of a SCWR is constant.
- Chemistry conditions such as pH can change the solubility of metal oxides in SCW. In SCWR, neutral species will probably be the dominant species of most corrosion products.
- The solubility of metal oxides can be affected by the concentrations of H_2 and O_2 dissolved in SCW. Literature data show that increasing H_2 or decreasing O_2 concentrations can reduce the concentration of dissolved metal species.

In general, the metal oxide solubilities reported in the literature were measured under much more aggressive conditions than those expected in an SCWR, e.g., in strongly acidic or alkaline solutions at pressures greater than 100 MPa. There is little solubility data under conditions relevant to an SCWR (300 to 625°C, 25 MPa, neutral to weakly alkaline pH) under different redox conditions. Few data exist for many metal oxides of significance to an SCWR, such as magnetite, hematite, nickel oxides and chromium oxides, under SCWR chemistry conditions; these data must be measured in order to aid in the selection of SCWR materials and to help define SCWR water chemistries.

5. References

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