THE SOLUBILITY OF MAGNETITE AND NICKEL FERRITE UNDER SUPERCRITICAL WATER REACTOR COOLANT CONDITIONS

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Abstract

Experimental data for the solubility of magnetite, hematite, nickel oxide and nickel ferrite, which are limited to temperatures below 300 °C and 10 MPa, have been critically evaluated. The results were used to construct a thermodynamic model for the solubility and hydrolysis of magnetite and nickel ferrite suitable for calculating oxide dissolution and transport in sub-critical and super-critical water (250-450 °C, 25 MPa). Our analysis shows that the iron (III) species, $Fe(OH)_4^-$, plays a particularly important role, and that both LiOH and ammonia have the potential to maintain pH in supercritical-water-cooled reactor coolants up to 400 °C. Shortfalls in the database, and experimental approaches to address these issues, are identified.

1. Introduction

The Generation IV CANDU® Supercritical-Water-Cooled Reactor (SCWR) is a conceptual design for a novel, extremely energy-efficient advanced reactor that would come on line after 2025. The Gen IV concept would produce supercritical water (SCW) at temperatures as high as 650ºC to generate electricity, hydrogen and district heating. The reactor and fuel channel concepts have been described by Torgerson et al. [1]. The use of SCW to carry heat from the reactor core to the turbine will generate much more extreme water chemistry conditions than those in current CANDU designs, which operate between 250 to 330ºC. In addition to extreme temperatures, the proposed CANDU-SCWR concept uses a direct cycle similar to current Boiling Water Reactor (BWR) designs, so that the water that drives the turbines will pass through the reactor core. Radioactive corrosion and fission products may form species sufficiently soluble in SCW to be transported to out of core piping or the turbines where they can deposit and give rise to high radiation fields.

The release and transport of corrosion products from the surfaces of system components has been a serious concern for all water-cooled nuclear power plants. The consequences of high levels of corrosion product transport are: a) increased corrosion product deposition on fuel cladding surfaces, leading to reduced heat transfer and the possibility of fuel failures, and b) increased production of radioactive species by neutron activation, resulting in increased out-of-core radiation fields and worker dose. The long-term viability of any Gen IV SCWR concept therefore depends on the ability of reactor developers to predict and control water chemistry, in order to minimize corrosion product and radionuclide transport. Because the SCWR will operate at pressures of 25-30 MPa, well above the critical pressure of water (p_c = 22.1 MPa), there will be no boiling and no “steam” phase. Instead, the coolant will undergo a transition from “water-like” to “steam-like” densities (from ~0.8 to 0.1 g/cm^3) as it passes from subcritical to supercritical conditions through the critical temperature at t_c = 373ºC

(Figure 1). Operating experience in supercritical thermal power stations has shown that the region of most importance is the range from 275 to 450ºC and 25 MPa, the so-called "pseudo transition zone" [2]. This is a frontier region of hydrothermal chemistry, both because the SCWR will produce unique water chemistry and because most quantitative studies of aqueous solutes do not extend above 300ºC. The implications of these chemistry conditions for corrosion product transport have yet to be fully elucidated. Above 450ºC, water is sufficiently steam-like that solid-gas thermodynamic models are likely to be adequate.

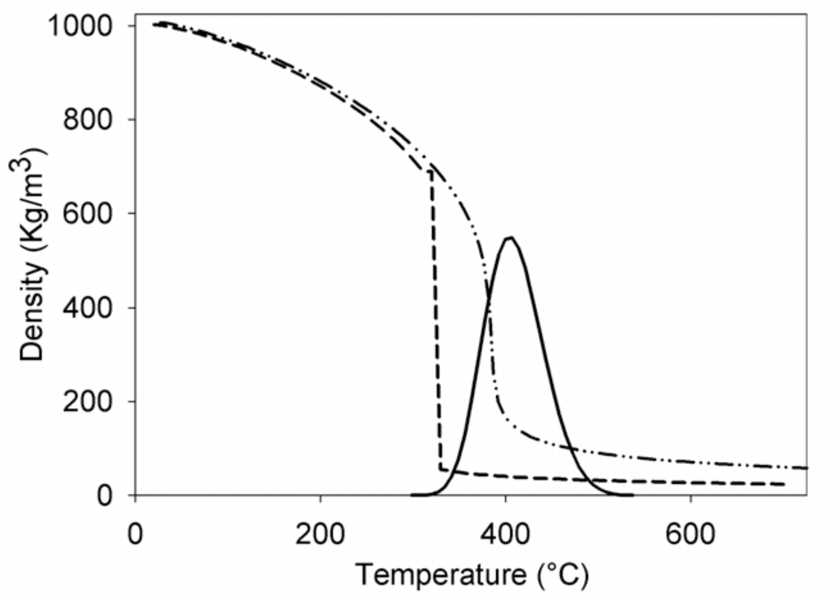

Figure 1: Density of water as a function of temperature. The solid line indicates the predicted region for corrosion product deposition.

2. Water Chemistry in Supercritical Power Plants

All-volatile treatment (AVT) is used in the feedwater systems of most subcritical and supercritical power plants. German work in the 1950s suggested an alternative which uses low conductivity water with oxygen added to stop flow-accelerated corrosion of the carbon steel piping and thereby reduce iron transport and deposition in the boiler tubes. Several water chemistry regimes are typically used in fossil-fired SCW plants [3, 4]: ammonia-hydrazine, hydrazine only, neutral pH plus added oxygen, and the combined treatment, consisting of injection of oxygen or hydrogen peroxide into the feed water to give 50-300 µg/kg dissolved oxygen plus addition of ammonia to give a moderately alkaline pH (pH between 8.0-8.5). No SCW plants use a non-volatile alkali such as KOH or LiOH for pH control, as is the practice in Pressurized Water Reactors (PWRs) and CANDUs. Most recent materials testing for the SCWR have used neutral water and low concentrations of dissolved oxygen. Table 1 summarizes some of the details on water chemistries used in supercritical power plants.

Table 1: All-Volatile and Oxygen Water Treatments used in Supercritical Power Plants

Water Chemistry	pH at 25ºC	Details	Reference
Ammonia + Hydrazine	-	0.7-1 mg amine/kg	[5]
	9.1 – 9.4	NH_3+N_2H_4	[6]
	8.5 – 9.5	NH_3	[7]
	9.1 – 9.6	-	[2]
	9.1	NH_3<0.8 mg/kg to avoid copper transport	[8]
	>9	NH_3 or cyclohexylamine + hydrazine	[4]
Hydrazine Only	8 – 8.5	N_2H_4 at 60-100 µg/kg	[6]
	7.7	N_2H_4 at 60-100 µg/kg	[9]
Chelate + NH_3 + N_2H_4	-	80 µg/kg chelate, 0.8 mg/kg ammonia, 0.2 mg/kg hydrazine.	[10]
	-	Increases thermal conductivity of iron oxide deposits	[11]
pH 7 with Oxygen	-	50-200 µg O_2/kg, conductivity <0.1 µS/cm	[5]
	6.5 – 7.3	-	[11]
	-	Reaction of $Fe(OH)_2$+O_2 slow compared to reaction with H_2O_2	[8]
	-	<0.15 µS/cm , 0.2-0.4 mg O_2/kg at boiler inlet	[12]
Combined Mode	8 – 8.5	NH_3+O_2 NH_3 provides slight buffering so that impurities do not cause wide swings in the pH, especially to the acid side where corrosion rates can increase	[13]

3. Predicting Activity Transport in a SCWR

The primary factors controlling corrosion product and activity transport in the primary coolant circuits of the current generation of CANDU reactors and PWRs are the solubilities of magnetite, Fe_3O_4, and nickel ferrite, $Ni_xFe_{3-x}O_4$. Magnetite and mixed ferrite solubilities decrease with temperature under acid conditions, causing precipitation in-core that leads to heavy fuel deposits and unacceptably high radiation fields. Raising the pH to slightly alkaline values causes the solubilities of these oxides to increase with temperature due to the presence of hydrolysed metal species of the form $Fe(OH)_2^0(aq)$ and $Fe(OH)_3^-(aq)$. The dissolution reaction includes both iron(II) and iron(III) species, and thus depends on the redox potential.

The challenges for SCWR chemistry are that neutral species such as $Fe(OH)_2^0(aq)$ and $Fe(OH)_3^0(aq)$ are expected to dominate in the supercritical region, and control of deposition using pH will become ineffective. The formation of neutral complexes increases with temperature, and can become important under near-critical and supercritical conditions; the most important region is from 300 to 450ºC where the properties of water change dramatically, and solvent compressibility effects exert a huge influence on solvation. With the exception of a few recent studies [14], the thermochemistry of neutral hydrolysed metal species needed to predict optimum coolant chemistry for the SCWR is poorly understood, even at temperatures well below the critical point.

4. The Solubility of Magnetite

Solubility experiments at high temperatures are exceedingly difficult to perform, and therefore calculation of the solubility of magnetite and other metal oxides from other thermodynamic data is an attractive alternative route to predict corrosion product deposition. The dominant reaction for the solubility of most metal oxides (Me_xO_y) where no oxidation-reduction (redox) reactions are involved is [14]:

$$({}^{1}/_{x})Me_xO_y(OH)_{xz-2y}(s) + ({}^{y}/_{x})H_2O \leftrightarrow Me(OH)_z^0(aq) \tag{1}$$

where the dissolution equilibrium constant K_s is:

$$K_s = \frac{a_{Me(OH)_z^0}}{a_{H_2O}^{\ y/x}} \tag{2}$$

The solubility equilibria often include redox reactions such as [15]:

$$Me(OH)_z^0 + H^+ \leftrightarrow Me(OH)_z^+ + {}^{1}/_{2}H_2(g) \tag{3}$$

$$Me(OH)_z^0 + {}^{1}/_{2}H_2 \leftrightarrow Me(OH)_z^- + H^+ \tag{4}$$

and stepwise hydrolysis reactions such as:

$$Me(OH)_z^0 \leftrightarrow Me(OH)_{z-q}^{q+} + qOH^- \tag{5}$$

$$Me(OH)_z^0 + nOH^- \leftrightarrow Me(OH)_{z+}^{n-} \tag{6}$$

These lead to a complicated series of reactions with many possible products. The overall equilibrium constant of these reactions can be calculated from the standard molar Gibbs energy of reaction, $\Delta_{rxn}G^o$,

$$\ln K = -\frac{\Delta_{rxn}G^o}{RT}, \tag{7}$$

and $\Delta_{rxn}G^o$ is calculated from the "apparent" standard molar Gibbs energies of formation (i.e. Gibbs energies of formation referenced to the elements at $T_r = 298.15$ K and $P_r = 100$ kPa).

$$\Delta_{rxn}G^o = \sum_{products} \Delta_{f,a}G_i^o - \sum_{reactants} \Delta_{f,a}G_j^o \tag{8}$$

The temperature dependence of K stems from the temperature dependence of $\Delta_{rxn}G^o$

$$\Delta_{f,a}G^{o}_{i(P,T)} = \Delta_{f}G^{o}_{i(\mathrm{Pr},Tr)} - S^{o}_{i(\mathrm{Pr},Tr)}(T - T_{r}) + \int_{Tr}^{T}(C^{o}_{P,i})_{\mathrm{Pr}}\,dT - T\int_{Tr}^{T}\frac{(C^{o}_{P,i})_{\mathrm{Pr}}}{T}\,dT + \int_{\mathrm{Pr}}^{P}(V^{o}_{i})_{T}\,dP \qquad (9)$$

By knowing the standard Gibbs free energy of formation and entropy at of each species at reference conditions, $\Delta_f G_i^o{}_{(\mathrm{Pr,Tr})}$ and $S_i^o{}_{(\mathrm{Pr,Tr})}$ respectively; the temperature dependence of the standard partial molar heat capacity, $C^o{}_{P,i}$; and standard partial molar volume, V_i^o, one can calculate the "apparent" Gibbs energy of formation $\Delta_{f,a}G^o{}_{i(\mathrm{Pr,Tr})}$ at the desired temperature and pressure [16].

Semi-empirical models and databases now exist for predicting the standard-state properties of aqueous electrolytes up to about 350 ºC and organic solutes up to 250 ºC [14,17]. Amongst these, one of the most practical methods is the Helgeson-Kirkham-Flowers (HKF) equation [18], which can be used to obtain a reasonable extrapolation to the supercritical region. When using extrapolated data, care must be taken to ensure that no unexpected species exist at reactor operating conditions before thermodynamic modelling in this region can be carried out with confidence. While parameters for transition metal hydrolysis and metal complexes are included in these databases, they have been derived from correlations based on a very limited number of accurate high-temperature experimental studies and should be used with great caution. A theoretical model for the properties of neutral ion-pairs in SCW has been reported by Kosinski and Anderko [19]; however, its accuracy is limited by a lack of experimental data and it is not applicable to dissociated ionic species. Such correlations are incorporated into several chemical equilibrium and mass transport models used by the electric power industry and the geochemical community, along with appropriate activity coefficient models. The principal limitations are: a) lack of thermodynamic and kinetic data for organic species above 250 ºC; b) lack of data and knowledge for associated ion-pairs, hydrolysed species and complexes above 250 ºC; c) shortcomings in theoretical models in the region 325-450 ºC where both ions and ion-pairs co-exist; and d) unknown species or reaction products that may exist over the high temperature range 300-650 ºC.

Accurate modelling of oxide and metal ferrite solubilities in the SCWR requires an entirely new, self-consistent database based on reliable experimental measurements. As a first step, work was done at the University of Guelph to develop such a self-consistent database for iron oxides and transition-metal ferrites, using critically evaluated literature data for oxide solubilities and other thermochemical data to obtain HKF parameters suitable for calculating Gibbs energies of reaction from Equations 7 to 9. The chemical equilibrium calculations that follow were done with the OLI Aqueous Modelling System, Version 7.0 (OLI Systems Ltd.). The parameters chosen for the original "public" database were based on those reported by Shock et al. [20], however these were found to be yield results that were inconsistent with CANDU reactor coolant chemistry operating experience. Instead, we developed a new model, based on the solubility data for magnetite and hematite reported by Tremaine and LeBlanc [15] and Diakonov et al. [21], respectively. The Tremaine and LeBlanc measurements were selected over other sources for magnetite solubilities because the data were measured over a wider pH range and hydrogen concentrations, giving added confidence in the fit. Additionally, the data of Tremaine and LeBlanc are consistent with more recent the data of Ziemniak et al. [22] for the majority of temperatures and pH values studied. Our approach is based on parameters for the iron (III) species $Fe(OH)_4^-$ determined from the hematite solubility data of Diakonov et al. [21]. Parameters for the iron

(II) species Fe^{2+}, $FeOH^{+}$, $Fe(OH)_2^0$ and $Fe(OH)_3^0$ were optimized to agree with the magnetite solubility data of Tremaine and LeBlanc [15], with the iron (III) species $Fe(OH)_4^-$ included, and with experimental values of $C^o_{P,i}$ for Fe^{2+}. The standard Gibbs free energies and entropies under ambient conditions are consistent with those used by Tremaine and LeBlanc [15]. The new database was used to extrapolate the solubility of magnetite to supercritical and near-critical conditions. The use of two pH buffers was explored, LiOH and ammonia. In all the calculations, reducing conditions corresponding to an initial concentration of 779 μmol/kg of hydrogen were maintained.

Figure 2 shows speciation of the aqueous species resulting from the dissolution of magnetite as a function of pH using LiOH as the pH-control agent at 250 ºC and 30 MPa. The solubility minimum occurs at neutral pH where neutrally charged species dominate. At low pH, cationic species dominate while at basic pH anionic species dominate. The major species present under current CANDU operating conditions are the iron (II) species $Fe(OH)_2^0$ and the iron (III) species $Fe(OH)_4^-$. The neutral and anionic iron (II) species $Fe(OH)_2^0$ and $Fe(OH)_3^-$ grow in importance as the temperature increases above 300 ºC, although the contribution of $Fe(OH)_3^-$ is *very* uncertain. These three species are therefore the most important for studies under supercritical conditions.

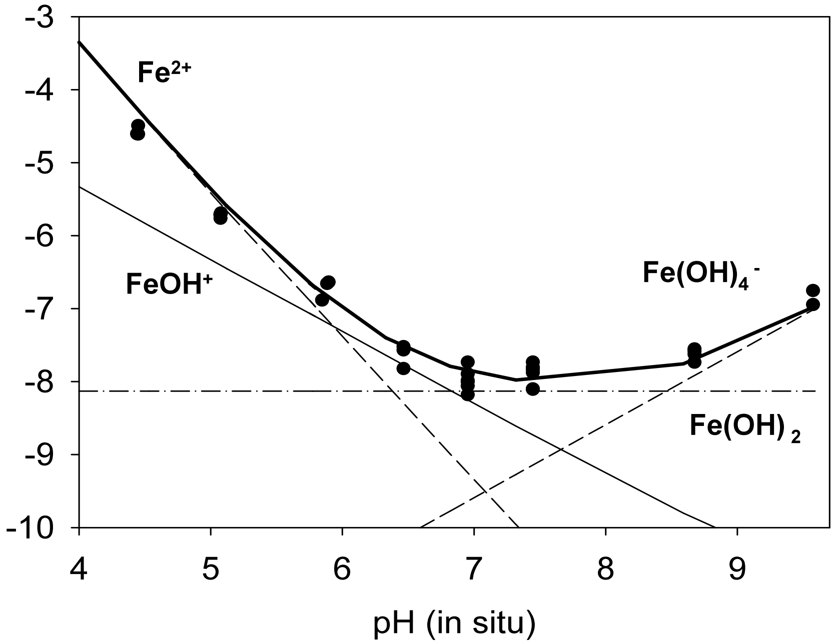

Figure 2. Speciation of magnetite at 250 °C as a function of equilibrium pH at 30 MPa with LiOH as the control agent.

The temperature dependence of the solubility of magnetite, when LiOH is used as a base, is plotted in Figure 3. Clearly, concentrations below ~250 µmol kg^{-1} are not sufficient to prevent the precipitation of magnetite as the fluid passes from the entrance of the reactor pressure tubes, at 250 °C, to higher temperatures as the coolant is heated in the reactor core. However, at concentrations above ~300 µmol kg^{-1}, it appears that LiOH can act as an effective pH control agent to ensure a positive solubility gradient of magnetite up to about 400 °C. At higher temperatures, magnetite will precipitate. Our calculation includes LiOH ion pairing effects, and the effect is due, in part, to ion-pairing and density effects. As noted above, the contribution of the anionic iron (II) species $Fe(OH)_3^-$, could not be extrapolated with confidence, and is assumed to be negligible.

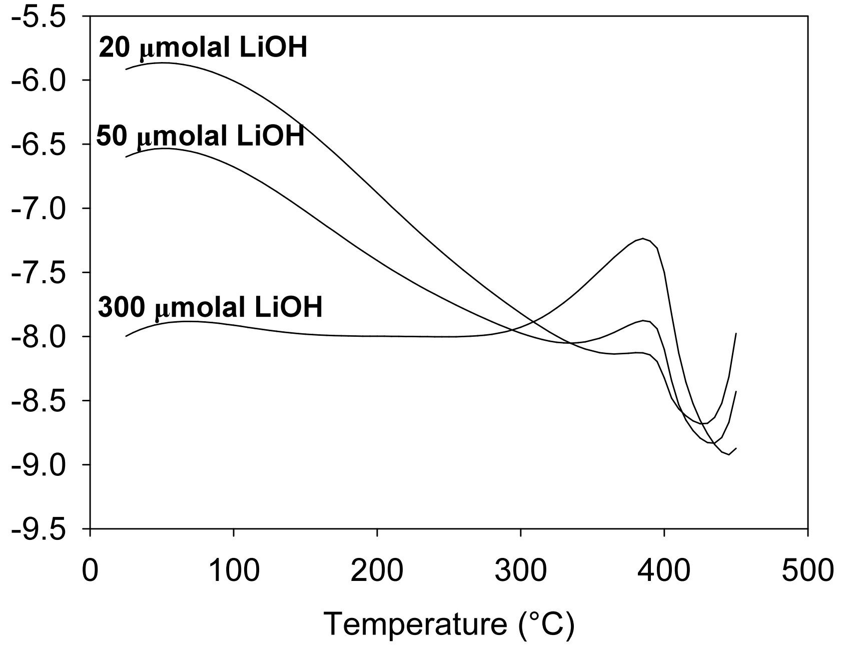

Figure 3. Total molality of iron resulting from magnetite as a function of temperature at 30 MPa for various LiOH concentrations using the HKF model.

The temperature dependence of the solubility of magnetite when ammonia is used as a pH control agent in water is plotted in Figure 4. For the calculations plotted in this figure, the contribution of Fe-NH_3 complexes was assumed to be negligible. Values for the equilibrium pH corresponding to the solutions shown in Figures. 2 and 4 are plotted in Figure 5.

Thermochemical data for the complexes of iron with ammonia have not been determined at these temperatures. In the calculations that follow, we have used a very approximate extrapolation, based on room-temperature data, for the species $Fe(NH_3)_4^{2+}$. The results are plotted in Figure 6. Although the behaviour of the hydroxy-complexes is similar to that in the previous calculations (See Figure 5), the dominant species in neutral and alkaline solutions is $Fe(NH_3)_4^{2+}$. This high concentration of the Fe-NH_3 complex causes the solubility to increase dramatically. It is important to note that these calculations are based on extrapolated room temperature data, and that polyvalent species are normally not stable in high-temperature water. However, these predictions are consistent with the measured iron release in ammoniated water chemistry shown in Figure 4. Clearly, an experimental study to determine formation constants for iron-ammonia complexes under SCWR conditions is an urgent priority.

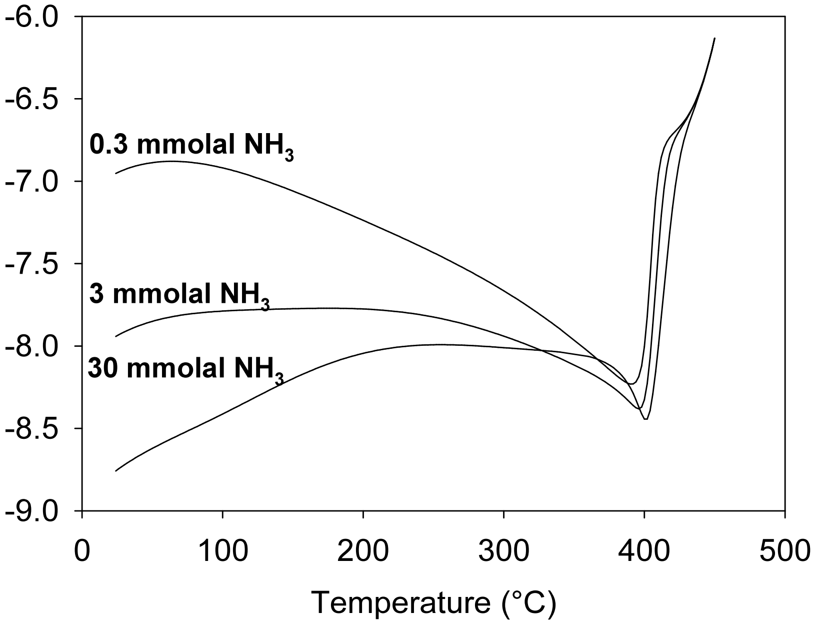

Figure 4. Total molality of iron resulting from magnetite dissolution as a function of temperature at 30 MPa, assuming Fe-NH$_3$ complexes are negligible.

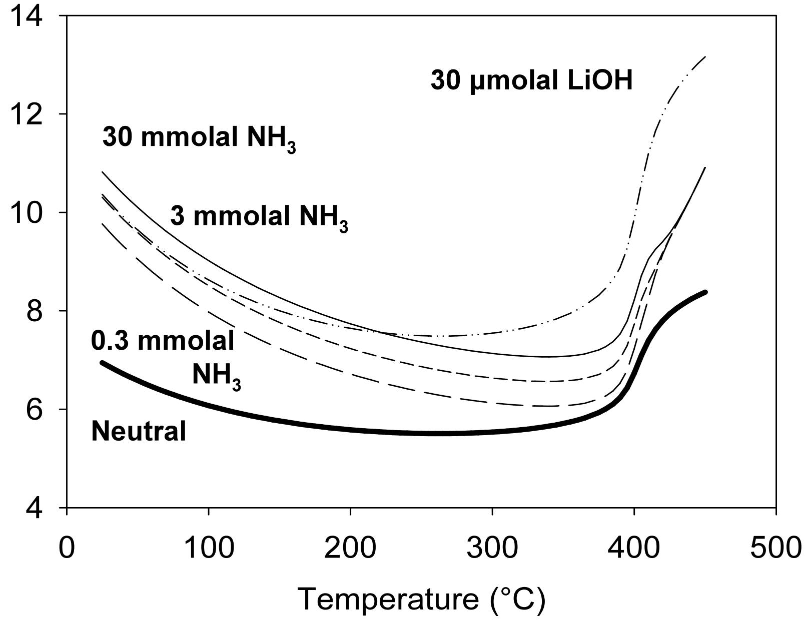

Figure 5. The equilibrium pH of the magnetite-saturated LiOH and ammonia solutions plotted in Figures 2 and 4.

Figure 6. Speciation of magnetite at 250 °C as a function of equilibrium pH at 30 MPa with ammonia as the control agent, when the $Fe(NH_3)_4^{2+}$ complex is included.

5. Nickel Ferrite Solubilities

Measurements on nickel ferrite are even more difficult, both because of all the experimental challenges listed above for magnetite, and because the surface composition of the equilibrating phase may be different than the bulk. Two experimental studies, reported by Sandler and Kunig at Westinghouse [23] and by Lambert and Lecompte at the CEN [24], both used flow methods. Sandler and Kunig's work meets most of the criteria outlined above. It appears to be well reported and carefully done. Moreover, the hydrogen dependence observed by Sandler and Kunig [23] would be consistent with the presence of iron (III) species in alkaline solutions, as was suggested by Tremaine and LeBlanc [15] and Ziemniak et al. [22] from their magnetite work. The major shortcoming study is that surface compositions of iron and nickel in the equilibrated ferrite were not reported. Lambert and Lecompte's work is reported in a short extended abstract at the BNES Conference in 1988 [24], so it is difficult to assess the quality of their data. A discussion of other papers on transition metal ferrite solubilities was done by Wesolowski et al. [14] in their critical review. They noted that studies by Ishigure et al. [25] ; Dinov et al. [26] and Hanzana et al. [27] did not all use controlled pH and that some of these saw hematite as a by-product which would have affected the interpretation of their results.

The approach taken in our work is similar to that reported above for magnetite. Briefly, the parameters for the nickel species were optimized to fit the solubility data reported by Palmer et al. (2002), and experimental standard partial molar heat capacities for Ni^{2+}. These data are being used, together with can the data reported by Sandler and Kunig [23] using an ideal solution model to describe non-stoichiometry in the nickel ferrite.

6. Conclusions

Plant data for iron oxide deposits inside boiler tubes of thermal stations operated with supercritical water show that the heaviest deposits can be expected at temperatures just above 400°C, where the density of supercritical water falls sharply. On the other hand, calculations show a significant drop in the solubility of magnetite around. Our calculations are consistent with this observation. This implies that the maximum in corrosion product deposition will occur within the core of an SCWR, at a well defined location, and raises the possibility of designing a easily cleaned "trap" for in core deposits. A major shortcoming in these calculations is the lack of formation constants for iron (II) hydrolysis and ammonia complexes, and nickel (II) ammonia complexes. There is a pressing need for experiments to determine accurate values for the pH-dependent solubility of magnetite and ferrites with well-characterized equilibrium pH, surface chemistry and redox conditions, up to and above the critical point of water.

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