

PREDICTING IRON TRANSPORT IN A SUPERCRITICAL WATER COOLED PRESSURE TUBE REACTOR

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Abstract

The long-term viability of a supercritical water-cooled reactor (SCWR) will depend on the ability of designers to minimize corrosion and the transport of corrosion products and radionuclides. This paper presents thermochemical calculations of the effect of two different pH control agents, LiOH and NH₃, on the solubility of magnetite under SCWR operating conditions. The HKF model was used to extrapolate thermochemical data for Fe(II) and Fe(III) aqueous species in the supercritical region, from which oxide and ferrite solubilities could be calculated. The results are being used to model iron corrosion product transport under SCWR conditions and to develop mitigating strategies.

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 650°C 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 330°C. 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 to 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/cm³) as it passes from subcritical to supercritical conditions through the critical temperature at $t_c = 373^\circ\text{C}$ (Figure 1). Operating experience in supercritical thermal power stations has shown that the region of most importance is the range from 275 to 450°C 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 300°C. The implications of these chemistry conditions for corrosion product transport have yet to be fully elucidated. Above 450°C, water is sufficiently steam-like that solid-gas thermodynamic models are likely to be adequate.

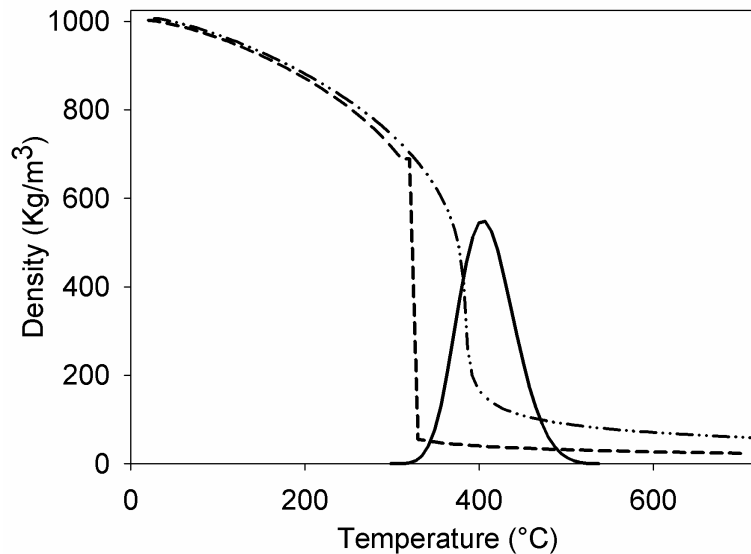


Figure 1 Density of water as a function of temperature. The solid line indicates the predicted region for corrosion product deposition.

2. Water chemistry in supercritical power plants

All-volatile water 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 carefully added oxygen addition 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 material testing programs 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 25°C	Details	Reference
Ammonia + Hydrazine	-	0.7-1 mg amine/kg	[5]
	9.1 – 9.4	NH ₃ +N ₂ H ₄	[6]
	8.5 – 9.5	NH ₃	[7]
	9.1 – 9.6	-	[8]
	9.1	NH ₃ <0.8 mg/kg to avoid copper transport	[9]
	>9	NH ₃ or cyclohexylamine + hydrazine	[10]
Hydrazine Only	8 – 8.5	N ₂ H ₄ at 60-100 µg/kg	[6]
	7.7	N ₂ H ₄ at 60-100 µg/kg	[11]
Chelate + NH ₃ + N ₂ H ₄	-	80 µg/kg chelate, 0.8 mg/kg ammonia, 0.2 mg/kg hydrazine.	[12]
	-	Increases thermal conductivity of iron oxide deposits	[13]
pH 7 with Oxygen	-	50-200 µg O ₂ /kg, conductivity <0.1 µS/cm	[5]
	6.5 – 7.3	-	[13]
	-	Reaction of Fe(OH) ₂ +O ₂ slow compared to reaction with H ₂ O ₂	[8]
	-	<0.15 µS/cm , 0.2-0.4 mg O ₂ /kg at boiler inlet	[14]
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	[15]

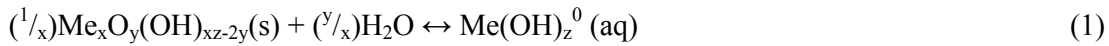
3. Predicting activity transport in a SCWR

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, Fe₃O₄, and nickel ferrite, Ni_xFe_{3-x}O₄. 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)₂⁰(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)₂⁰(aq) and Fe(OH)₃⁻(aq) are expected to dominate in the supercritical region, so that control of deposition using pH will become ineffective. The most important region is from 300 to 450°C 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 [16], the thermo-

chemistry 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.

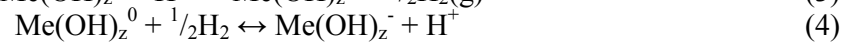
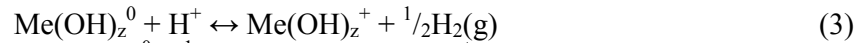
Solubility experiments at high temperatures are exceedingly difficult, and therefore calculation of the solubility of magnetite and other metal oxides from other thermodynamic data is a route to predict corrosion product deposition and minimize the need for experimental work. The dominant reaction for the solubility of most metal oxides (Me_xO_y) where no oxidation-reduction (redox) reactions are involved is [16]:



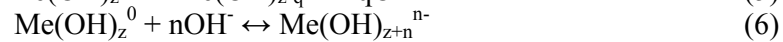
where the dissolution equilibrium constant K_s is:

$$K_s = \frac{a_{\text{Me}(\text{OH})_z^0}}{a_{\text{H}_2\text{O}}^{y/x}} \quad (2)$$

The solubility equilibria often include redox reactions such as [17]:



and stepwise hydrolysis reactions such as:



These lead to a complicated series of reactions with many possible products. The overall equilibrium constant of these reactions can be calculated from

$$\ln K = -\frac{\Delta_{\text{rxn}} G^0}{RT} \quad (7)$$

where:

$$\Delta_{\text{rxn}} G^0 = \sum_{\text{Products}} \Delta_f G_i^0 - \sum_{\text{Reactants}} \Delta_f G_j^0 \quad (8)$$

The temperature dependence of K stems from the temperature dependence of $\Delta_{\text{rxn}} G^0$.

$$\Delta_{f,a} G_{i(P,T)}^0 = \Delta_f G_{i(\text{Pr},T_r)}^0 - S_{i(\text{Pr},T_r)}^0 (T - T_r) + \int_{T_r}^T (C_{i,P}^0)_{\text{Pr}} dT - T \int_{T_r}^T \frac{(C_{i,P}^0)_{\text{Pr}}}{T} dT + \int_{\text{Pr}}^P (V_i^0)_T dP \quad (9)$$

By knowing the standard free energy of formation and entropy at reference conditions, $\Delta_f G^0(\text{Pr}, T_r)$ and $S_{i(\text{Pr},T_r)}^0$ respectively, and the temperature dependence of the standard partial

molar heat capacity, C_p° , and standard partial molar volume, V° , one can calculate the free energy of each species at the desired temperature and pressure [18].

Several models exist for predicting the temperature and pressure dependence of standard thermodynamic properties of aqueous species. Amongst these, one of the most practical methods is to use the Helgeson-Kirkham-Flowers (HKF) equations [19]. The HKF model can be used to obtain a plausible extrapolation to the supercritical region, using the HKF parameters for the hydrolysis products of iron(II) and iron(III). However, the possibility of the formation of unexpected species needs to be explored before thermodynamic modelling in this region can be done with confidence. The chemical equilibrium calculations that follow were done with the OLI Aqueous Modelling System, Version 7.0 (OLI Systems Ltd.).

In order to optimise the accuracy of current available databases for iron oxide solubility, an entirely self-consistent database, based on the most reliable experimental measurements, was assembled. In this way, errors caused by using inconsistent data are eliminated, and the HKF parameters obtained provide an accurate fit to the data. The parameters chosen for the database were based on those reported by Shock et al. [20]. However, parameters for the iron(III) species $\text{Fe}(\text{OH})_4^-$ were fitted to the solubility data of Diakonov et al. [7]. Additionally, the standard state free energy and entropy under ambient conditions were optimized to agree with the magnetite solubility data of Tremaine and Leblanc [17]. The Tremaine and Leblanc measurements were selected over the other sources as these authors measured the solubility over a wider pH range, thereby giving added confidence to the fit. Additionally, the data of Tremaine and Leblanc have been found to provide much better agreement with data from Ziemniak et al. [21] for the majority of temperatures and pH values.

The 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 hydrogen were maintained at $779\mu\text{mol/kg}$.

4. Results

4.1 LiOH

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 350°C 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 $\text{Fe}(\text{OH})_4^-$ and $\text{Fe}(\text{OH})_3^-$. The iron(II) neutral species $\text{Fe}(\text{OH})_2^0$ grows in importance as the temperature increases. These species are therefore the most important for studies under supercritical conditions.

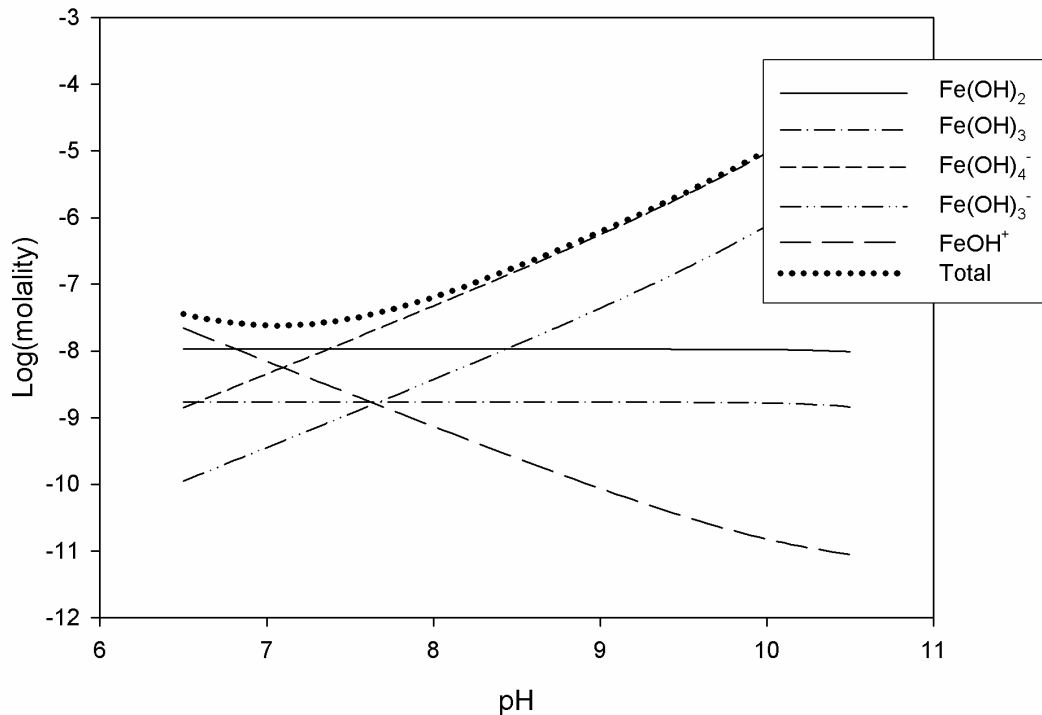


Figure 2 Speciation of magnetite at 350°C as a function of pH at 30 MPa with LiOH as the control agent.

Figure 3 shows the temperature dependence of the solubility of magnetite at three concentrations of LiOH, centered around the value used in CANDU-6 coolant. As the concentration is raised from 2×10^{-5} to 5×10^{-5} mol/kg, the temperature dependence of the solubility between 250 and 300°C changes from negative to positive. Experience in all CANDU-6 and earlier reactor types has shown that a positive solubility gradient is required to prevent in-core deposition of magnetite and high ^{60}Co radiation fields. LiOH is soluble in supercritical water and, although its dissociation constant decreases with temperature, our calculation shows that it is sufficiently basic to maintain a positive solubility gradient up to about 400°C. Above this temperature, the solubility of magnetite drops dramatically, because of the sharp drop in the density of water (See Fig. 1). *A major finding of this work is that LiOH is apparently suitable as a pH control agent up to these conditions.*

4.2 NH_3

The temperature dependence of the solubility of magnetite when ammonia is used as a pH control agent in water is plotted in Figure 4. In this figure, Fe-NH₃ complexes have been ignored. Ammonia is a much weaker base than LiOH but its dissociation constant is more temperature dependent in this range. Thus, although the pH is lower, the temperature dependence of the magnetite solubility is similar to that observed with LiOH and it is positive at all three ammonia concentrations examined. Moreover, higher concentrations of NH₃ provide a lower solubility of magnetite and therefore might reduce thinning and corrosion. This would be offset by the problems associated with higher ^{13}N radiation fields.

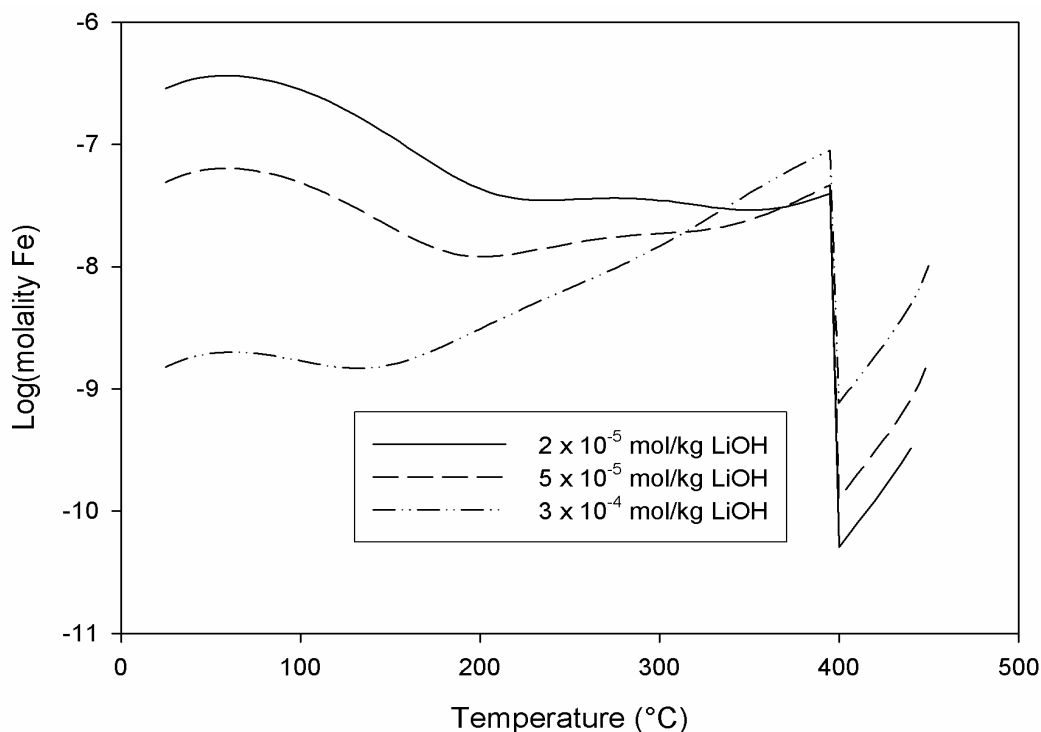


Figure 3 Total molality of iron resulting from magnetite as a function of temperature at 30 MPa for various LiOH concentrations

Thermochemical data for the complexes of iron with ammonia have not been determined at these temperatures. In the calculations that follow, we have used the extrapolations tabulated in the OLI "Public" database, without checking their source. Although the behaviour of the hydroxy-complexes is similar to that in the previous calculations, here the dominant species is $\text{Fe}(\text{NH}_3)_4^{2+}$. This high concentration of the Fe-NH₃ complex causes the solubility to increase dramatically. The temperature dependence of the solubility is shown in Figure 6. It is important to note that this data is based on extrapolated room temperature data, and that polyvalent species are normally not stable in high-temperature water. Clearly, an experimental study to determine formation constants for iron-ammonia complexes under SCWR conditions is an urgent priority.

5. 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 experimental data for pH-dependent solubility of magnetite and ferrites with well-characterized equilibrium pH and redox conditions, and formation constants for hydrolysis and ammonia complexes.

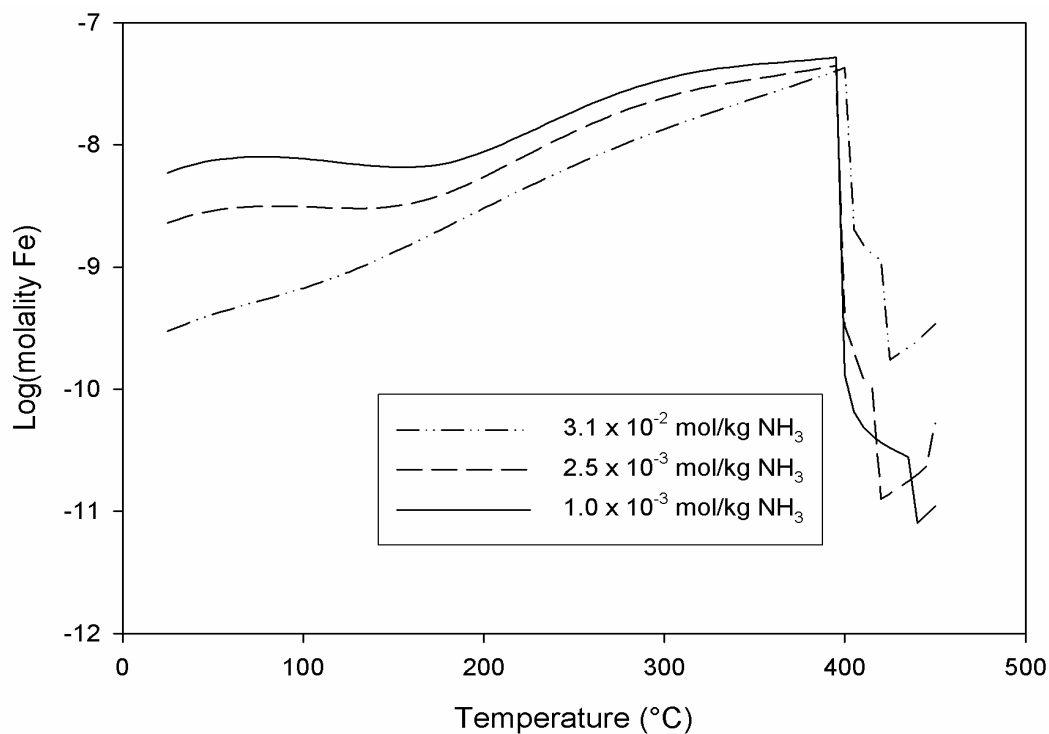


Figure 4 Total molality of iron resulting from magnetite dissolution as a function of temperature at 30 MPa and various ammonia concentrations, ignoring Fe-NH₃ complexes.

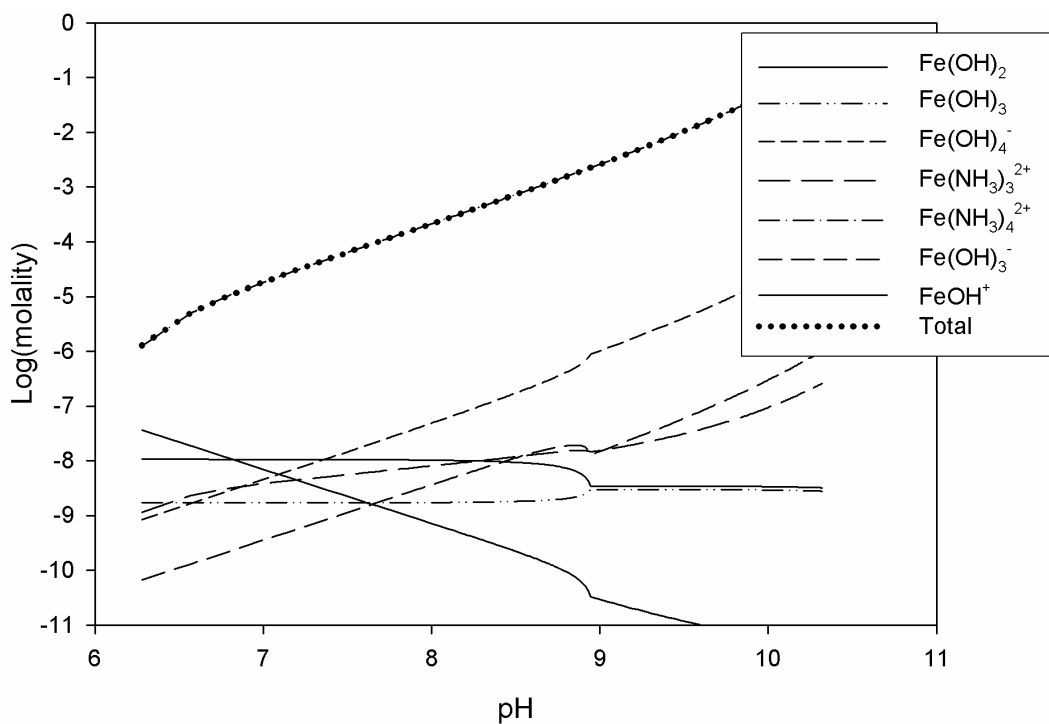


Figure 5 Speciation of magnetite at 350°C and 30 MPa as a function of pH with ammonia as a control agent. The calculation includes iron-ammonia complexes.

6. Acknowledgements

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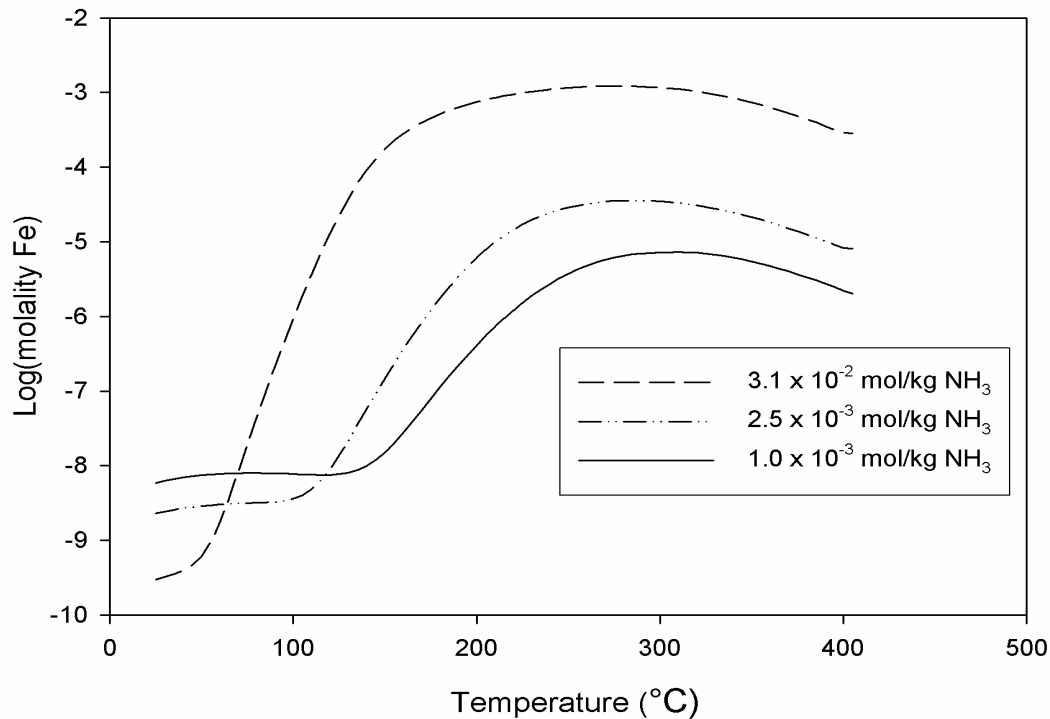


Figure 6 Total molality of iron as a function of temperature at 30 MPa and various concentrations of NH_3

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