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M. P. Srinivasan and S. V. Narasimhan
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BHABHA ATOMIC RESEARCH CENTRE
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60   Abstract :A short review of solubility of corrosion products at high temperature in either neutral or alkaline water as encountered in BWR, PHWR and PWR primary coolant reactor circuits is presented in this report. Based on the available literature, various experimental techniques involved in the study of the solubility, theory for fitting the solubililty data to the thermodynamic model and discussion of the published results with a scope for future work have been brought out.

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Solubility of Corrosion Products in High Temperature Water

M.P.Srinivasan and S.V.Narasimhan

Water and Steam chemistry laboratory

Applied Chemistry Division

Bhabha Atomic Research Centre

IGCAR Campus, Kalpakkam, Tamil Nadu 603 102

Introduction:

Metal oxides dissolve and deposit in the primary circuit of pressurised water reactors(PWR) and pressurised heavy water reactors(PHWR). The PWR coolant contains dissolved hydrogen, boric acid and lithium hydroxide. The solubility of the corrosion products depends on the concentrations of these three additives, which vary through the reactor cycle and also on the temperature, which varies with the location in the circuit. These parameters are generally believed to be responsible for the net transport of corrosion products from one part of the circuit to another and for the transport of radioactivity from the core to out of core surfaces[1,2].

The corrosion product oxides which form on the primary circuit surfaces contain metals such as Cr, Mn, Fe, Co and Ni. However their quantity is dictated by the inventory, structural surfaces, release rates and chemistry environment. Calculation of the solubility of these oxides by a thermodynamic model is necessary to understand the mechanism of corrosion product transport and parameters controlling the same. Establishing the thermodynamic quantities for such a model requires measurements of solubilities of oxides on a wide range of oxide compositions and temperatures. The thermodynamic models derived from these studies have been used to calculate two quantities relevant to coolant chemistry specification for minimising

corrosion product transport and activity transport. They are:

1) The pH of minimum solubility and

2) The pH at which the temperature coefficient of solubility is zero.

However, a thermodynamic model of magnetite or mixed spinel solubility is of limited use in modelling corrosion product transport if dissolution and deposition are not limited by fluid phase mass transfer. When this process is not rate limiting, rate constants for the surface reactions are needed if the corrosion product transport model is to be quantitative. In addition knowledge about selective leaching of metals is also rquired. In order to achieve this, measurements of dissolution and deposition rates of crud in high temperature boric acid/ lithium hydroxide solutions were carried out by Balakrishnan[3] and Thornton[4].

The present review collates the extensive work carried out by different authors in this direction. A compilation of the experimental procedures followed by them and a comparison of their data is brought out. Scope for future investigations is also discussed.

Experimental procedures

Described below are the experimental facilities employed by Sandler, Lambert, Balakrishnan and Tremaine amongst various others.

Sandler etal[5,17] in their study of solubility of nickel ferrite used a teflon lined make up tank containing an aqueous solution of boric acid and lithium hydroxide. The solution was degassed to ensure less than 5ppb of dissolved O_2 concentration. A small portion of the pressurised circulating solution was first passed through a millipore filter and then through a small

diameter platinum alloy tubing to a heated twin chamber pressure vessel in an electric furnace. In the first chamber four rolls of platinum mesh separated by horizontal spacers catalysed the removal of residual traces of oxygen with dissolved hydrogen. The second chamber was the reaction vessel and contained approximately 20 gm of nickel ferrite powder on top of a platinum filter. The pressure vessel was made of titanium and was lined with 0.5mil thick 90%Pt-10%Ir alloy.

The solution finally left the top of the reaction chamber through a platinum filter. It then passed over an injector point where a small amount of hydrochloric acid was injected to keep the dissolved iron and nickel in solution. After leaving the heated zone, the solution passed through a second millipore filter ($0.05\mu m$) before it entered the flow restricters. These consisted of 0.1mm i.d. platinum alloy capillaries of various lengths (several meters) and served to restrict the flow to different rates between 4 and 0.4 cm^3/min. The solution passed through a glass vessel containing a pH microelectrode and then entered two cation-exchange columns in series where iron and nickel ions were collected for later elution and analysis. Iron was analysed colorimetrically as ferrous phenanthroline complex and nickel was analysed as dimethyl-glyoxime complex spectro-photometrically.

Lambert et al[6] in their study of influence of hydrogen pressure on the solubility of magnetite in aqueous solutions used a static titanium autoclave equipped with a magnetic stirrer. About 5gm of Fe_3O_4 and 500 cm^3 of solution were introduced in the pressure vessel and after evacuation the chosen hydrogen pressure was established (6 atm at 25°c except for studies pertaining to the influence of hydrogen pressure). Samples were taken through a titanium filter after decantation and mixed with a known volume of standard nitric acid to avoid reprecipitation. Dissolved iron was determined colorimetrically immediately after sampling to prevent the dissolution of small particles passed through the filter.

Balakrishnan[3] used a technique in which the aqueous solution was first passed through a column packed with the radioactive oxide (made active by neutron irradiation), whose dissolution was to be studied. The solution was then passed through another column packed with a high temperature ion exchange material. Magnetite, a good high temperature ion exchange material, was the obvious choice for the study of dissolution of magnetite. Even for most other oxides present in the primary circuit (such as Fe_2O_3 or oxides of cobalt and nickel including ferrites) magnetite could act as an efficient ion exchanger since it can incorporate into its lattice the ions produced from the dissolution of these oxides. The dissolved active ions from the first column were exchanged for inactive iron ions in magnetite in the second column. The latter was counted over a Ge (Li) gamma spectrometer to determine the concentration of the species dissolved from the oxide in the first column. Solubility was obtained from the concentration of the dissolved oxide from first column at a slow flow rate of the solution through the column. (The slow flow rate was defined as the maximum flow rate below which the solubility did not change with flow rate). For most of the experiments the aqueous solution was presaturated by passing through the inactive oxide similar to the one under study packed in a column to eliminate the concentration gradient acting as a driving force for dissolution. Therefore the rate of exchange of active ions between the irradiated oxide and the aqueous solution under this condition represented the dissolution rate under equilibrium conditions.

Tremaine and Leblanc[7] used an experimental apparatus in which H_2-saturated solution of HCl or NaOH from a polyethylene reservoir was pumped through a thermostated cell containing about 85 gm of Fe_3O_4 (1.0 m^2 surface area). Dissolved iron from the saturated solution was then precipitated in the condenser or collected by the cation-exchange resin, still under high pressure. At the end of a run, the iron was eluted from the resin and condenser with HCl. Iron was analysed by atomic absorption spectroscopy. Three such flow systems were run in parallel with solution fed from a common pump and reservoir. Except for the stainless steel and oxidized zirconium surfaces in the pumping system, the entire apparatus was constructed

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of titanium. A line was included bypassing each condenser and cation-exchange resin to allow the oxide to be equilibrated with flowing solution at the temperature of interest before beginning to collect iron from the saturated solution. Whenever feed solutions saturated with hydrogen over pressures in excess of 1 atm were required, a high pressure stainless steel reservoir was used.

Theory

Procedures for fitting magnetite solubility data to a Thermodynamic Model[8]:

The dissolution equilibria for the various hydroxo species of ferrous and ferric may be represented by an equation of the form

$$1/3\ Fe_3O_4 + (z\text{-}b)\ H^+ + (4/3\text{-}z/2)\ H_2 = Fe(OH)_b^{(z\text{-}b)} + (4/3\text{-}b)\ H_2O \tag{1}$$

The total iron solubility depends on the equilibrium constants $K_{z,b}$ where z is the charge on Fe namely 2 for ferrous and 3 for ferric and b is the number of OH$^-$ groups. The total concentration of all iron species is given by

$$C_s = \Sigma^{z,b}\ [Fe(OH)_b^{(z\text{-}b)+}] \tag{2}$$

$$= \Sigma^{z,b}K_{z,b}\cdot[H^+]^{(z\text{-}b)}\cdot\Gamma_1^{(z\text{-}b)}p_{(H2)}^{(4/3\text{-}z/2)}/\Gamma_{z\text{-}b} \tag{3}$$

where Γ_q is the activity coefficient of species with charge q and $p_{(H2)}$ is the partial pressure of hydrogen. The equilibrium involving dissociation of water is represented as

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$$K_w = [H^+] [OH^-] \Gamma_1^2 \tag{4}$$

where $[H^+]$ is obtained from the charge balance equation given below:

$$[H^+] - K_w/[H^+]\Gamma_1^2 + (z-b)\Sigma^{z,b} [Fe(OH)_b^{(z-b)+}] + [Li^+] = 0 \tag{5}$$
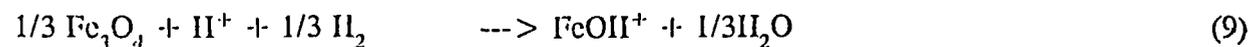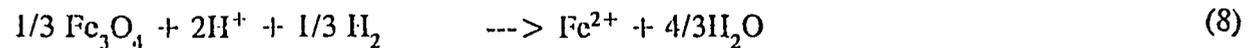
$[Li^+]$ represents the base ion molality. If K^+ or NH_4^+ ions are used, sum of the concentrations of the base cations are to be used. In the case of strongly acidic solution the negative of the acid molality is to be employed). However each equilibrium constant $K_{z,b}$ in equation (3) obtained from

$$-RT\ln(K) = \triangle G(T) \tag{6}$$

$$= G(T_0) - S(T_0).\{T-T_0\} - Cp.T.\ln(T/T_0) + Cp(T-T_0) \tag{7}$$

where T_0 is usually taken as 298 K, R is the gas constant, G free energy, S entropy and C_p specific heat at constant pressure. Thus it is possible to compute C_s from first principles making use of values for the various thermodynamic quantities.

Other authors have carried out analysis of solubility data following the same approach. Sweeton and Baes[9] have analysed magnetite solubility data in terms of the following reactions involving four ferrous species
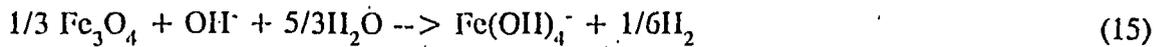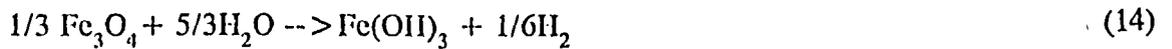
$$1/3\ Fe_3O_4 + 2H^+ + 1/3\ H_2 \quad \text{---}> \quad Fe^{2+} + 4/3H_2O \tag{8}$$

$$1/3\ Fe_3O_4 + H^+ + 1/3\ H_2 \quad \text{---}> \quad FeOH^+ + 1/3H_2O \tag{9}$$

$$\frac{1}{3} Fe_3O_4 + \frac{2}{3} H_2O + \frac{1}{3} H_2 \quad \text{---}> \ Fe(OH)_2 \tag{10}$$

$$\frac{1}{3} Fe_3O_4 + OH^- + \frac{2}{3} H_2O + \frac{1}{3} H_2 \text{---}> Fe(OH)_3^- \tag{11}$$
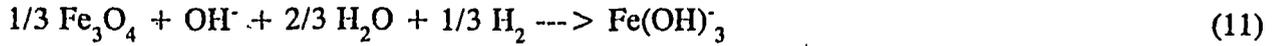
The total solubility of iron may thus be written as

$$C_s = \Sigma^3_{i=0} \ [Fe(OH)_i^{(2-i)+}] \tag{12}$$

$$= p_{H2}^{1/3} \ [K_{2,0}[H^+]^2 \ \Gamma_1^2/\Gamma_2 + K_{2,1}[H^+] + K_{2,2} +$$
$$K_{2,3} K_W/[H^+]\Gamma_1^2 \tag{13}$$

where p_{H2} is the effective partial pressure of H_2 gas in the solution.

Magnetite solubility data of Tremaine and Leblanc[10] have been analysed using reaction scheme involving both ferrous and ferric species in solution. Ferric species were assumed to be important only in alkaline solution and were accounted for by the following reactions.

$$\frac{1}{3} Fe_3O_4 + \frac{5}{3}H_2O \text{ --}> Fe(OH)_3 + \frac{1}{6}H_2 \tag{14}$$

$$\frac{1}{3} Fe_3O_4 + OH^- + \frac{5}{3}H_2O \text{ --}> Fe(OH)_4^- + \frac{1}{6}H_2 \tag{15}$$

In addition all the ferrous species as considered by Sweeton and Baes are also included. Hence the solubility is defined as:

$$C_s = \Sigma^3_{i=0}[Fe(OH)_i^{(2-i)+}] + \Sigma^4_{i=3}[Fe(OH)_i^{(3-i)+}] \tag{16}$$

$$= \{H_2\}^{1/3} [K_{2,0}[H^+]^2 \, \Gamma_1^2/\Gamma_2 + K_{2,1}[H^+]$$
$$+ K_{2,2} + K_{2,3}K_w/[H^+]\Gamma_1^2]$$
$$+ \{H_2\}^{-1/6} [K_{3,3} + K_{3,4} \, K_w/[H^+]\Gamma_1^2] \tag{17}$$

Thornton etal[11] defined the solubility ratio as the ratio of concentration in the liquid to the concentration in the solid by analogy with the definition of the distribution coefficient. Consider a solid compound ABC. Equilibrium for component A is acheived when, $\mu_A^S = \mu_A^{Sol}$ where μ_A^S and μ_A^{sol} are the chemical potentials of A in the solid and solution respectively. Since, $\mu = \mu_0 + RT\ln \Gamma x$ where μ_0 is the chemical potential of pure A in the standard state, the solubility ratio may be expressed by

$$X_A^{Sol}/X_A^S = \Gamma_A^S/\Gamma_A^{Sol} \exp (\mu - \mu_0)/RT \tag{18}$$

where X = mole fraction

Solubility ratio derived on the assumption of first order rate constant yields X_A^{Sol}/X_A^S $= k_{Ar}/k_{Ad}$ where k_{Ar} and k_{Ad} are rate coefficients for release and deposition of A respectively.

At relatively low temperatures of interaction ($\leq 300°C$) solid state diffusion is expected to be slow and and thus it is highly desirable to ensure that less than a monolayer dissolves during the course of the measurements. Subsequently the surface composition should be checked to make sure the absence of any change. If these two criteria are not satisfied there would be some uncertainty in the value of X_A^S.

Modelling of dissolution process (Balakrishnan)[3]

Consider a volume element of length dx in the active oxide column at position x along the length of the column in the direction of flow of the solution. The solution which is saturated in the metal ion at concentration C_s, with a specific activity of a_x at this point enters the volume element at a flow rate m and leaves it at the same rate. The metal ion concentrations do not change. However there is an increased specific activity $(a_x + da)$. The active metal ions are released from the oxide at a rate $K.d\alpha$ where K is the rate constant and $d\alpha$ the surface area of the oxide in the volume element. If the specific activity of the active oxide is A and the rate of release of activity is $K.A.d\alpha$

The dissolved ions are deposited on to the oxide at a rate of k.s.ds which corresponds to an activity deposition rate of $k.s.a_x.dx$ where k is the rate constant, s is the solubility. For a column of length L with a weight of oxide w, and a specific surface area σ for the oxide:

$$d\alpha = w\sigma dx/L \qquad (19)$$

The specific activity a_L when the solution leaves the column will be

$$a_L = A(1-e^{-Kw\sigma/ms}) \qquad (20)$$

For a unit volume of solution passed during experiment the activity collected on the ion exchange column will be

$$s_1 = s(1-e^{-Kw\sigma/ms}) \qquad (21)$$

The term s_1 can be considered as an apparent solubility since it is obtained by dividing the

activity per unit amount of solution by the specific activity of the active oxide. Since the above equation contains only the ratio of the specific activities, radioactive decay during the experiment will not affect the calculated solubility, provided that the specific activities are corrected for the same time.

The equation (21) can be solved to find the solubility s and the dissolution rate constant K of the oxide by carrying out the experiment with at least two flow rates.

The pH values for minimum solubility and zero temperature dependence of solubility of magnetite and Nickel ferrite.

The equilibrium for the unhydrolysed ferrous ion for magnetite solubility is given by equation (8). Hence:

$$Fe^{2+} = K_{2,0}[H^+]^2[p_{H2}]^{1/3} \tag{22}$$

Similarly for the ferric species in equation (1), the following equilibrium is valid.:

$$1/3 Fe_3O_4 + 3H^+ = Fe^{3+} + 1/6 H_2 + 4/3 H_2O \tag{23}$$

$$[Fe^{3+}] = K_{3,0}[H^+]^3[p_{H2}]^{-1/6} \tag{24}$$

The total iron solubility C_s is given by the sum of all the solution species

$$C_s = [Fe^{2+}]\{1 + K_{2,1}{}^H/[H^+] + K_{2,2}{}^H/[H^+]^2\}$$

$$+[Fe^{3+}]\{1+K_{3,1}{}^{II}/[H^+]+K_{3,2}{}^{II}/[H^+]^2+K_{3,3}{}^{II}/[H^+]^3\} \qquad (25)$$

using equation (22) and (24)

$$C_s = [Fe^{2+}]\,f_2 + [Fe^{3+}]\,f_3 \qquad (26)$$

$$C_s = r_{2,0}p_{H2}{}^{1/3}.H^2f_2+K_{3,0}p_{H2}{}^{-1/6}.H^3.f_3 \qquad (27)$$

where H stands for $[H^+]$ and f_2 and f_3 are the hydrolysis terms defined in equation (25). The dependence of hydrolysis constants for Fe(II) and Ni(II) are given in Fig(1). The values obtained from this figure can be used to solve the above equations to obtain the solubility.

The pH for minimum iron solubility for magnetite is obtained by differentiating equation (27) with respect to hydrogen ion concentration, setting this to zero and solving the resulting equation, i.e. $(dC_s/dH)_T=0$ yielding the desired value of H^+. Since $K_{2,0}$ and p_{H2} are independent of H^+, the solution is readily found.($K_{a,b}$:equilibrium constants, where a denotes the charge on the ion and b denotes the number of hydroxyl ions)

These equations become complex in the case of non-stoichiometric nickel ferrite. They can be expressed as a series of equation one for each of the soluble nickel and iron species(Sandler and Kunig[5]). Considering only ferrous and nickel species a typical equation is:

$$Ni_xFe_{3-x}O_4 + A.H^+ + B.H_2 = i_aNi(OH)_a{}^{(2-a)+}$$

$$+ j_bFe(OH)_b{}^{(2-b)+} + Ni_{x-i}Fe_{3-j-x}O_c + D.H_2O \qquad (28)$$
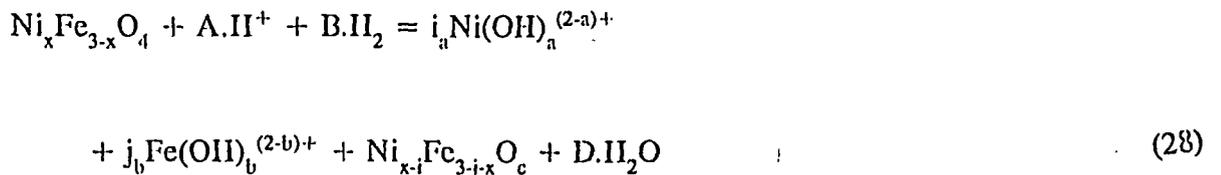
Where a and b take values 0,1,2,3. i_a and j_b are the stoichiometric coefficients for nickel and

iron. A,B,C,and D are constants which can be expressed as a function of i_a, j_b by balancing hydrogen atoms, oxygen atoms and electric charge and by assuming that the ratio of the trivalent to divalent atoms in the spinel remains constant.

The law of mass action for the unhydrolysed ferrous ion and the unhydrolysed nickel ion obtained by putting a=b=0 in equations(28) and suitably modifying the coefficients A and B yields

$$[Fe^{2+}] = K_{2,0} [H^+]^A p_{H_2}^B / [Ni^{2+}] \qquad (29)$$

Equation (29) has different dependences on hydrogen ion concentration and hydrogen partial pressure as compared to that of magnetite equation (27). Furthermore, there is a dependence on nickel ion concentration. Thus the solubility of iron obtained from equations (33) and hydrolysis constants, by summing over the solution species of iron (both ferrous and ferric species) differs from the form of equation for magnetite in several respects.

For nickelferrite one must expect a different solution since the following parameters differ for magnetite and nickel ferrite

a)The ratio $K_{2,0}/K_{3,0}$

b)Power dependence of H^+ from equation (27) or (29)

c)presence or absence of aqueous nickel concentration in the relationship

The above conclusion is contrary to that of Lindsay[12] who considered that the pH for

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minimum solubility should be identical for magnetite and ferrites owing to the identical hydrolysis equilibria for aqueous iron species. However, Lindsay neglected ferric species and omitted consideration of the possible effect of aqueous nickel species on the solubility of iron with respect to nickel ferrite.

The pH for zero temperature dependence of iron solubility is obtained by differentiating equations (27) and (29) with respect to temperature. The locus of zero temperature coefficient of iron solubility at 565 K for magnetite is given in Fig(2).

$$dC_s/dT = 0 \qquad\qquad (30)$$

This will result in a different pH value for magnetite than for nickel ferrite for the reasons outlined above. Since positive temperature coefficient is desirable the scatter in the measured values of temperature coefficients is quite significant, the % probability of positive temperature coefficient is expressed as a function of pH or Li concentration as a mark of acceptable temperature coefficient. Fig(3) gives a typical comparison of temperature coefficients of iron solubility at 565 K.

Results and discussions:

Tremaine and Leblanc's[7] fit include both ferrous and ferric species, whereas Sweeton and Baes fits include only ferrous species. The H_2 dependences of solubility for ferrous and ferric species follow a $H_2^{1/3}$ and $H_2^{-1/6}$ dependence respectively in these two cases. Comparison of predicted magnetite solubility with variation in temperature is given in (Fig 4).

The various investigators have used both hydrochloric and boric acids and sodium, potassium and lithium hydroxides. It is generally agreed that solubility is a function of solution pH and not dependent upon the acid anion or alkali cation provided that the weakly acidic

priate concentration of boric acid and lithium hydroxide, even where the solution used a different acid or alkali for comparing different studies.

Comparison between Tremain and LeBlanc's[7] and Sweeton and Baes[9] solubility data for magnetite at 300°C shows for both a minimum pH_{300} at 7.0 ± 0.3. The reproducibility of the measurements in each study is typically within a factor 4 or 5 and that values measured by different workers differ by upto a factor ~10. Sweeton,Mesmer and Baes[13] correlation is intended for use over the temperature range of the measurements($\leq 300°C$). This correlation is the one used by Tremaine and Leblanc[10] and differs only very slightly from the K_w values(Cobble[14],) used by Sweeton and Baes[9]. The other option is Marshall and Franck's[15] correlation which is intended for extrapolation of the thermodynamic fits above 300°C and gives appreciably different K_w values from those of Sweeton etal[13].

EFFECT OF HYDROGEN

Besides Lambert[6] etal, Kunig and Sandler[16] have also studied the dependence of solubilities of magnetite and ferrite on H_2 concentration (Fig.5). At high concentration both display ~1/3rd power law for iron solubility dependence around 300°C. At low H_2 concentrations($\leq 400\mu m$) iron solubility from the ferrite becomes independent of p_{H2}. The latter behaviour is attributed to the formation of vacancies in the ferrite lattice caused by dissolution of Fe^{2+} ions which cannot be replaced by Fe^{3+} ions as this requires consumption of H_2.

Values of solubility experimentally obtained by Lambert[6] etal near room temperature are rather low, which they explained as possibly due to the slow rate of reduction of Fe^{3+} by H_2 and by the competing reaction of precipitation of $Fe(OH)_3$. Moreover this mechanism would be responsible for the decrease of the mean size of magnetite crystals in aqueous solutions and for the small influence of hydrogen pressure at low temperature.

Solubility of Ni ferrites:

The value for nickel solubility from $Ni_{0.6}$ ferrite determined by Kunig and Sandler[16] is $\bar{}10^{-8}$ mole/kg H_2O near pH_{300} 6.5 and pH_{300} 8.5, but goes through a sharp minimum near pH_{300} 7.5. Extrapolation of low-temperature data for NiO indicates a sharp solubility minimum near 300°C.(at pH_{300} 6.4), the value being 6.10^{-6} mole/kg. The minimum solubility of nickel from the ferrite is at least two orders of magnitude below this value. Their values for the solubility of iron from the nickel ferrite in solutions of LiOH and $B(OH)_3$ in the pH_{300} region of 6.5 to 7.5 are only slightly lower than those found by Sweeton and Baes for magnetite in KOH solutions. A lower solubility is to be expected due to the lower concentration of iron.

The dissolution of nickel ferrite is generally incongruent; the solubility of nickel is normally much lower than that which corresponds to its proportion in the ferrite. Nevertheless,the composition of the ferrite is essentially unaffected by the dissolution in the course of the experiments , because the total amount dissolved is very small.

Co-Ni ferrites: $[Co_zNi_yFe_xO_4]$

Kunig and Sandlers[16] cobalt solubility data are very scattered. The data show the same solubility dependence on dissolved hydrogen concentration as observed for iron. Co(III)is a very powerful oxidising agent which is not found in water unless stabilised by complex formation. It is most likely that the observed hydrogen dependence reflects the interdependence of iron, cobalt and nickel solubilities rather than the presence of Co(III)in solution . The data were fitted to the same model as for nickel with cobalt solubility proportional to its concentration in the lattice. The cobalt solubility from the two cobalt nickel ferrites studied (Y=0.22, Z=0.24 and Y=0.5 ,Z=0.05)are very nearly superimposable despite the factor of five dif-

ference in cobalt content of the lattice Fig(6). It is possible that these data are in fact the measured solubility of a cobalt oxide in the ferrite. This would explain the lack of dependence of solubility on lattice cobalt concentration but not the observed hydrogen dependence. For nickel, the solubility is not expected to depend on the hydrogen concentration, although there are no data to confirm this.

Co-Mn-Ni ferrites

Thronton[4] used a packed bed flow technique to study the rates of dissolution and deposition and the equilibrium solution concentration of cobalt and manganese dissolving from a sample of mixed ferrites obtained as a PWR corrosion product in boric acid-lithium hydroxide solutions containing dissolved hydrogen at 300°C. ($Co_{0.0062}Ni_{0.32}Mn_{0.16}Cr_{0.88}Fe_{1.65}O_4$). Equilibrium solution concentrations and first order rates of dissolution and deposition were obtained by fitting the solution concentration vs flow rate data to the following expression $C_m=C_0(1-\exp(-kW\sigma/m))$ where C_m is measured solution concentration(mol kg^{-1}), C_0 is equilibrium solution concentration (mol kg^{-1}), K is deposition rate constant (kg m^{-2}s^{-1}), W is mass of oxide in the sample column(g), σ is oxide specific surface area (m^{-2}g^{-1}) and m is the flow rate through the column(kg s^{-1}). (C_0 and k were adjustable parameters.)

Both cobalt and manganese equilibrium solution concentration show the expected decrease in concentration with increasing pH and there is evidence for a concentration minimum in the pH range 7-8 in both cases (Fig.7). There is substantial uncertainty on the location of the minimum equilibrium solution concentration but the best fit value is pH_{300} ~7.8 and ~7.4 for Co and Mn respectively. The oxide lattice and the presence of other cations should influence solubility behaviour. The solubility and hydrolysis constants derived thus do not have their usual rigorous thermodynamic meaning and they are best regarded as empirical parameters. Cobalt and manganese do not appear to dissolve congruently from the lattice of the oxides

studied. The congruency ratio is defined as:

$$\frac{[Co]_{soln}/[Co]_{oxide}}{[Mn]_{soln}/[Mn]_{oxide}}$$

The dimensionless ratio has a value $^-0.075$ at $pH_{300}\ ^-7$, indicating that Co is less likely than Mn to dissolve from the lattice. In the absence of better thermodynamic data on the solid phase the reason for this is uncertain..

The deposition rate constants for manganese and cobalt solution species are very similar in magnitude. The best fit overall deposition rate constants appear to have maximum values at $pH_{300}\ ^-6.2$ for both cobalt and manganese. One has to consider the nature of the solution species and the oxide surface to understand why the deposition velocity should pass through a maximum. At low pH, the solution species are predominantly the divalent cation and its first hydrolysis product, while the negatively charged third hydrolysis product becomes more important at higher pH. Hence at higher pH, the oxide surface will be more negatively charged than at low pH. Protons and hydroxyls act as potential determining ions at the oxide-water interface thus:

$$H_3O^+ + MOH_s = M(H_2O)_s + H_2O$$

$$OH^- + MOH_s = MO^- + H_2O$$
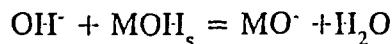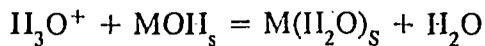
where s denotes a surface species. Positively charged surface groups predominate at low pH and negatively charged groups predominate at higher pH. Since the solution species must approach the surface to deposit, they will experience an electrostatic interaction with the

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charged interface. At low and high pH, this will be more repulsive than at some intermediate value; however the pH of maximum deposition velocity does not necessarily coincide with point of zero charge of the oxide. The maximum in the deposition rate constant is thus probably electrostatic in origin.

Future work

Quantitative understanding of corrosion product transport requires data on the kinetics of oxide dissolution and deposition. At temperatures much above ambient only very little data is available in this area. Balakrishnan and Thornton have measured rates of net isotope exchange at an essentially equilibrium surface which is inconsistent with fluid phase mass transfer rate. Dissolution of mixed spinels is generally not congruent and consequently, changes in composition occur at the surface of the oxide crystals. In a flowing system, the surface of the spinel is invariably not at equilibrium with the oxide bulk and consequently, the equilibrium thermodynamic solubility cannot be measured. On the contrary it is only the equilibrium solution concentration rather than solubility that is measured and used for subsequent discussions. Hence mixed spinel solubility should be studied by making use of Balakrishnan's method. To study the equilibrium thermodynamic solubility, a theoretical model and experimental procedure has to be developed.

Further experiments must be performed to study surface structures of magnetite under different hydrogen pressure and temperature conditions.

Data are not available on chromium solubility from Cr containing ferrites.

The oxide studied by Thornton[4] has a lower tendency to release cobalt into solution compared with an earlier study of synthetic cobalt -nickel ferrites by Kunig[11] et al. The ratio $(S/x)_K/(S/x)_T$ where S is equilibrium solution concentration and x is Co stoichiometry in the lattice has an average value of 61 but could lie in the range 28 to 135. More experiments on cobalt nickel ferrite solubility have to be carried out to know the origin of variation in solubility and to remove the large uncertainities in the results.

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Figures included in this report have been adapted from the following references with the permission of the authors.

Fig 1 - Ref 11 - p55
Fig 2 - Ref 1 - p42
Fig 3 - Ref 1 - p43
Fig 4 - Ref 1 - p38
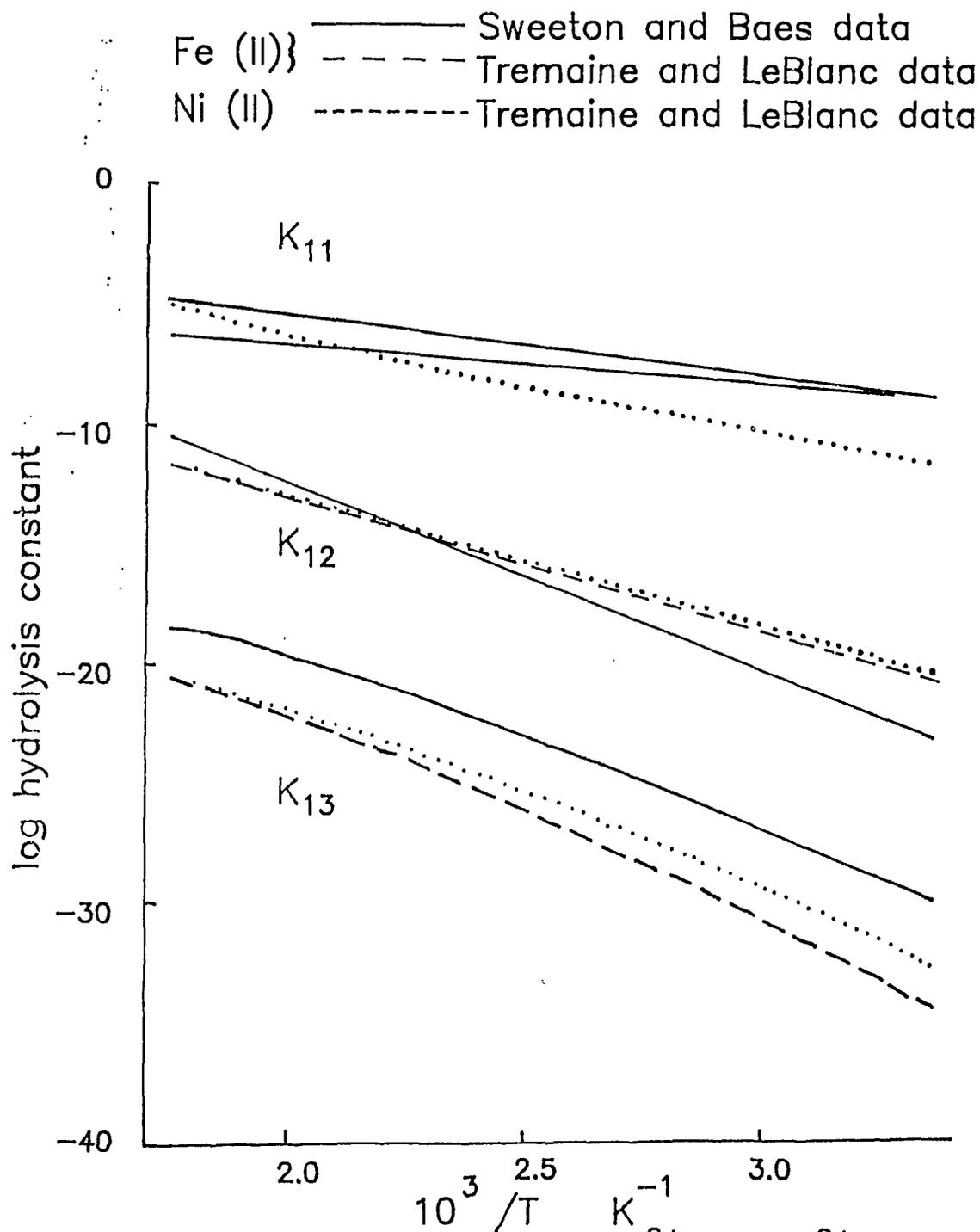Fig 5 - Ref 1 - p39
Fig 6 - Ref 8 - p71
Fig 7 - Ref 4 - p31

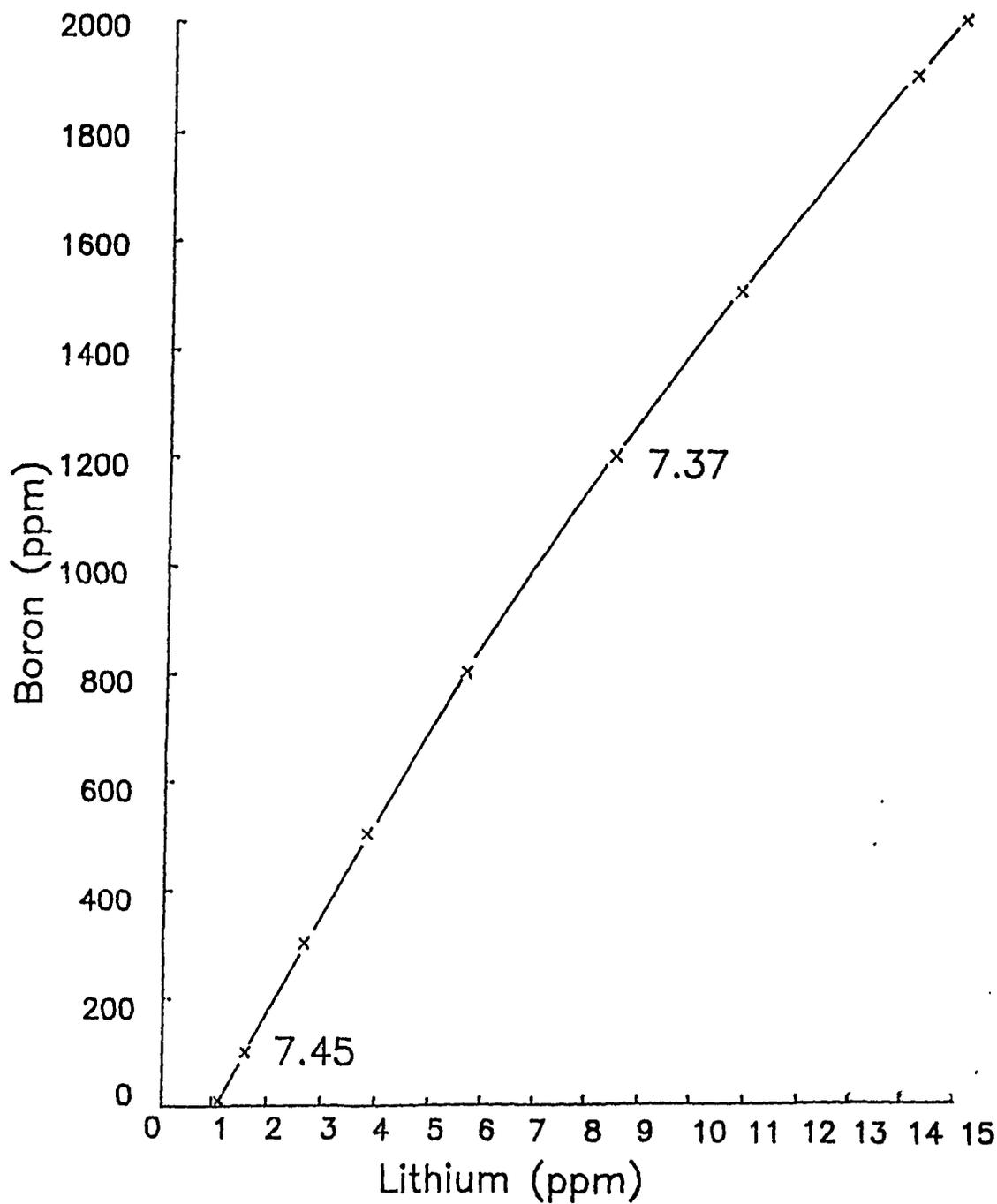Fig.1 Hydrolysis constants for Fe^{2+} and Ni^{2+} Cations 298 — 573K.

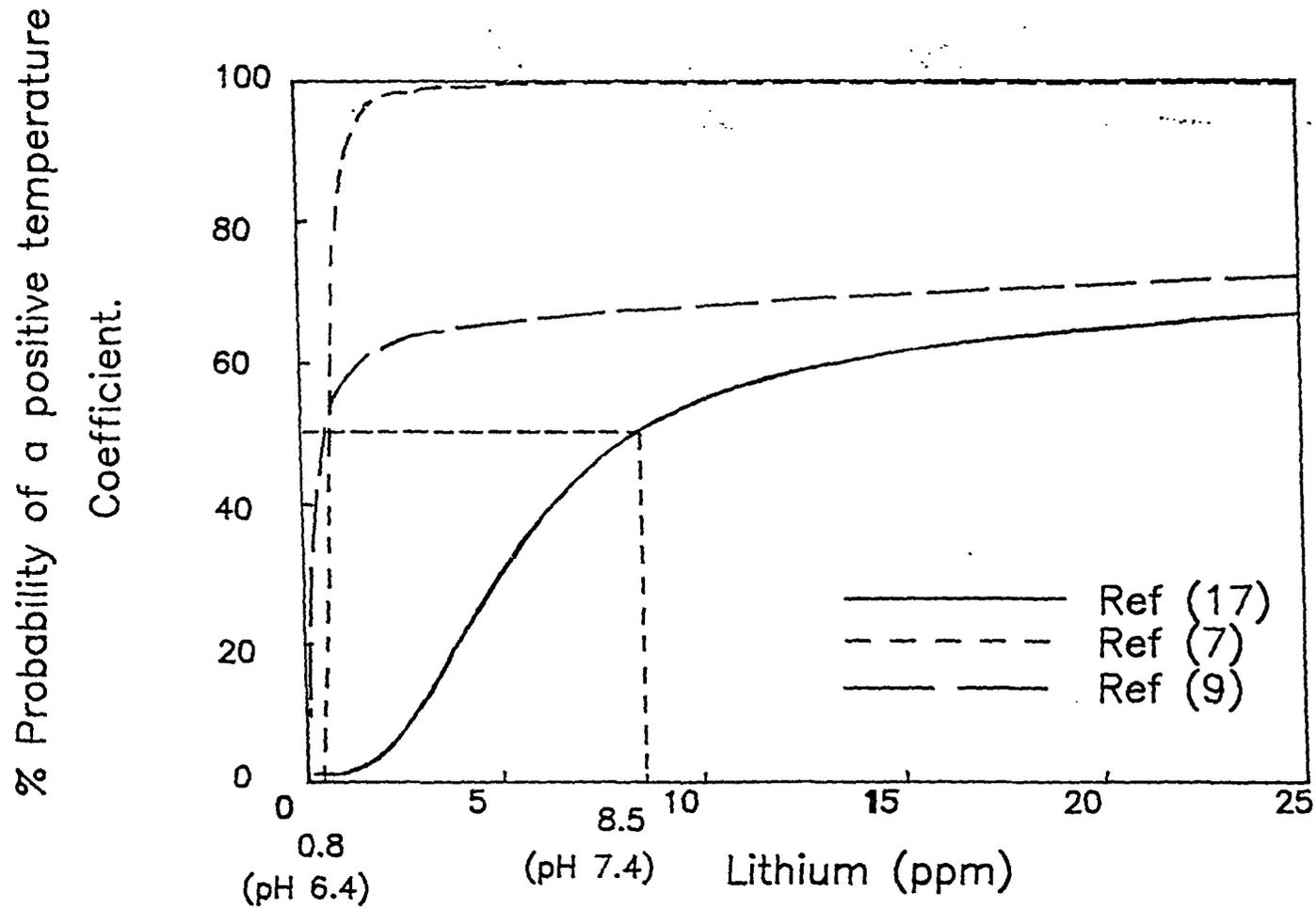Fig.2 Locus of Zero Temperature Coefficient of Iron Solubility (565K, 1200 umolal H_2)

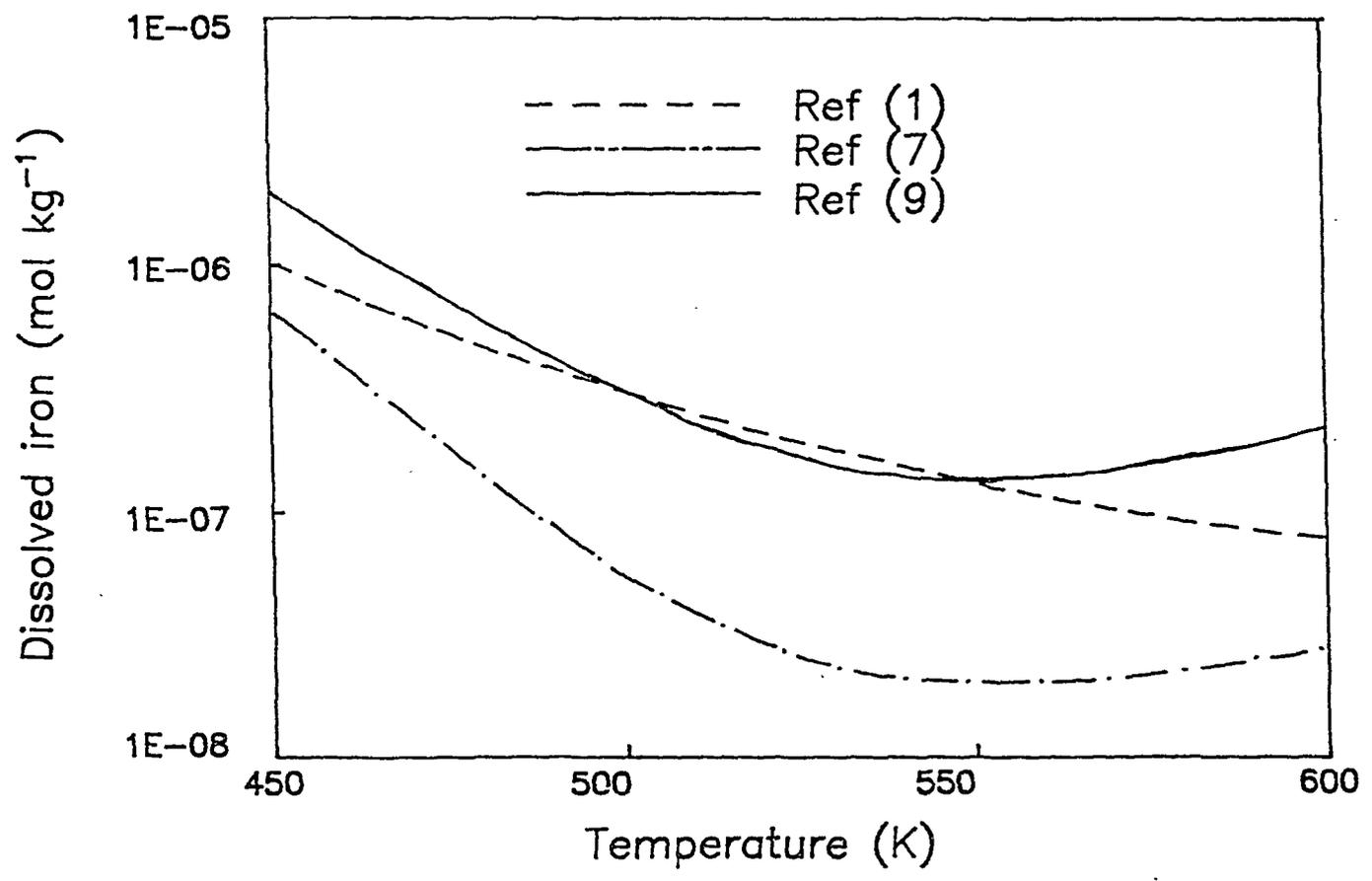Fig.3 Comparison of Temperature Coefficients of Iron Solubility at 565K (1200 ppm Boron).

Fig.4 Comparison of Predicted Magnetite Solubility from Three Studies
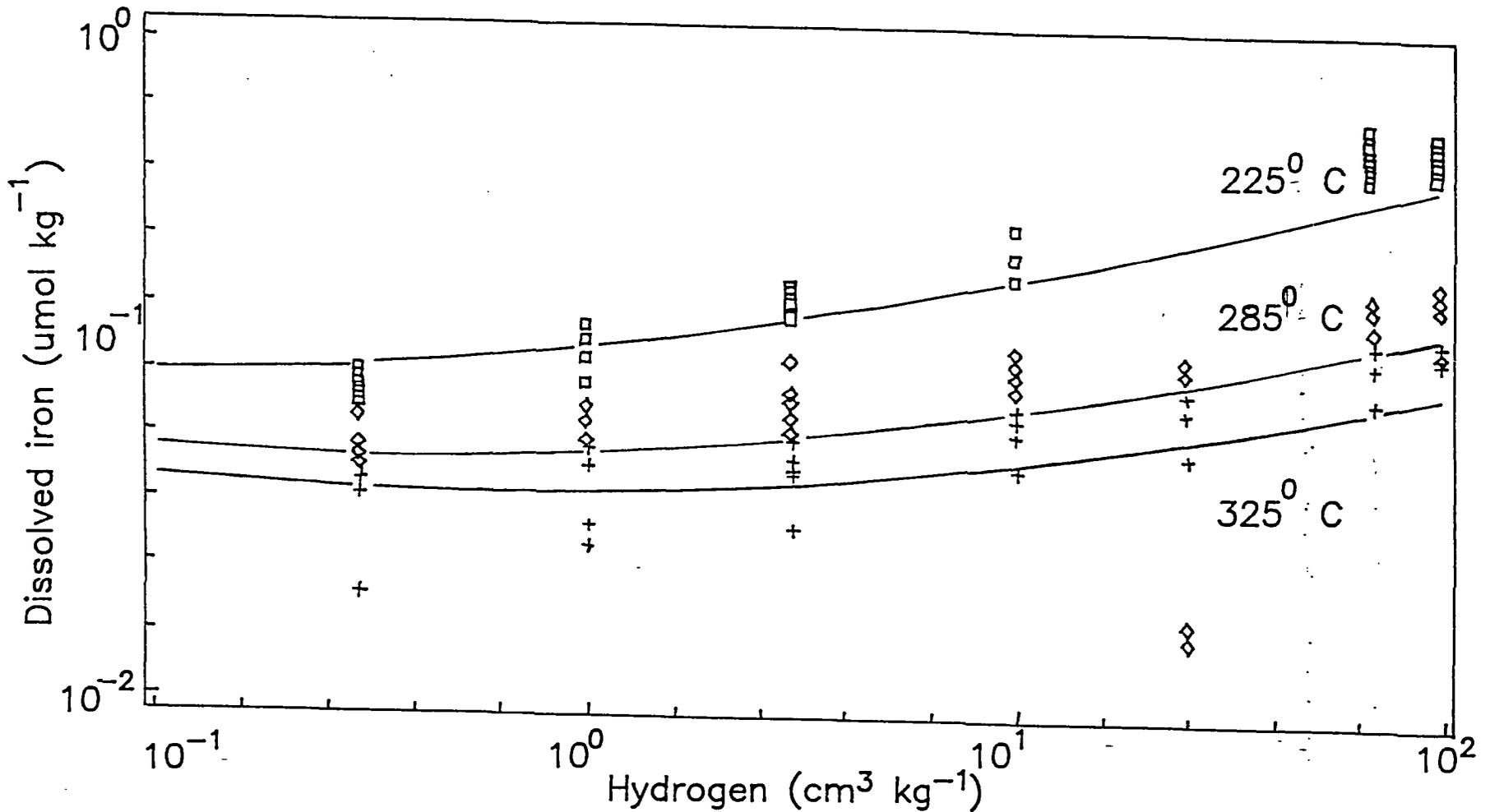1200 umolal H_2, 0.7 ppm Lithium, 650 ppm Boron.

Dissolved iron (umol kg^{-1})

10^0

10^{-1}

10^{-2}

225^0 C

285^0 C

325^0 C

10^{-1}

10^0

10^1

10^2

Hydrogen (cm^3 kg^{-1})

Fig.5 Iron Solubility from Fe$_{2.45}$ Ni$_{0.5}$ Co$_{0.05}$ O$_4$ as a function of
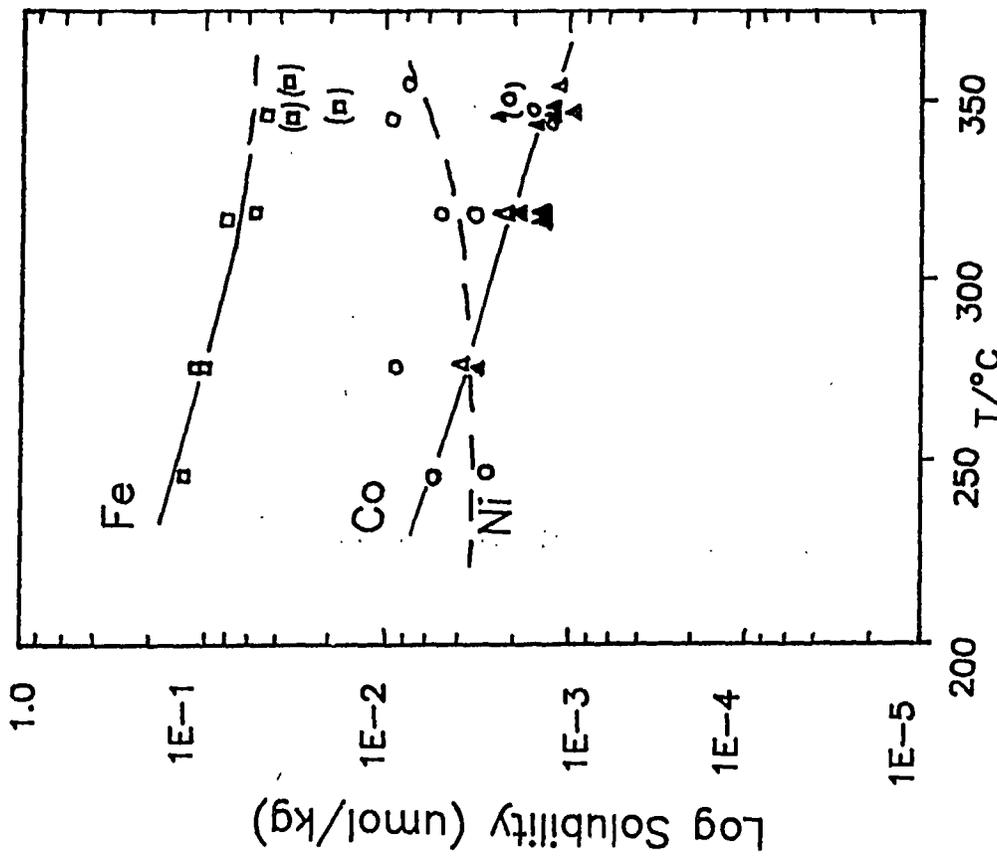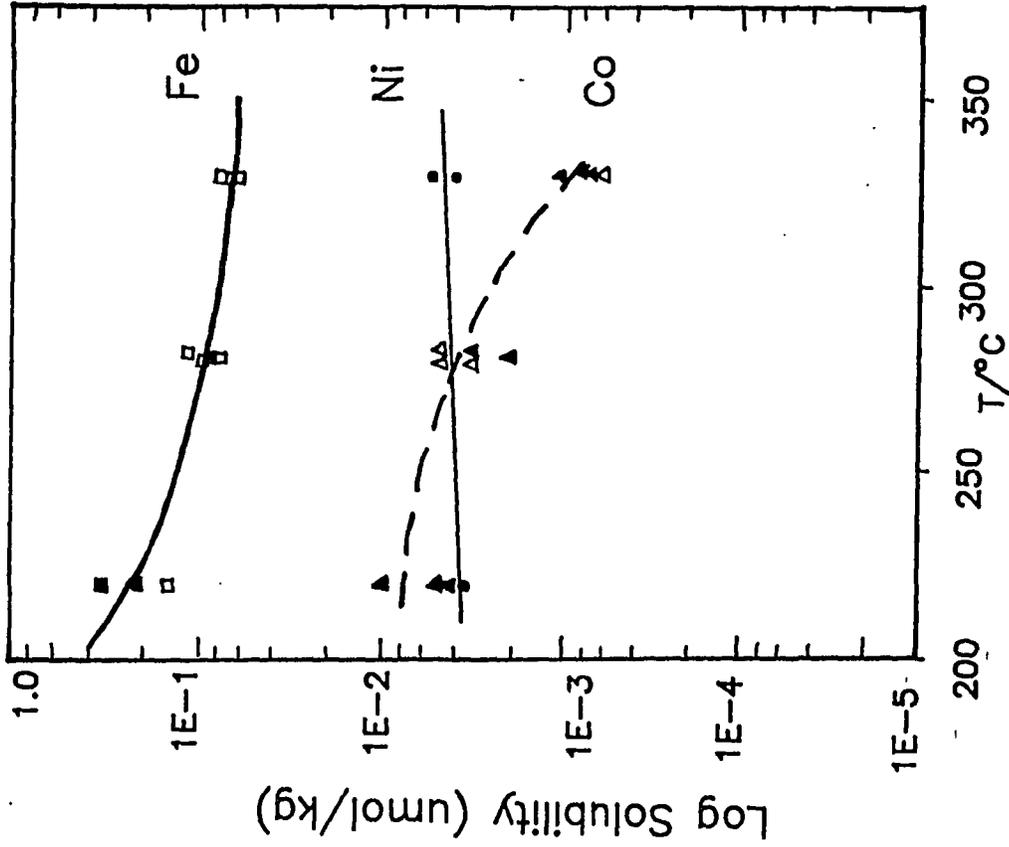Hydrogen Concentration (650 ppm B, 0.7 ppm Li)

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Solubility of $Ni_{0.22}$ $Co_{0.24}$ $Fe_{2.54}$ O_4 in 0.06 M H_3BO_3 + 10^{-4}M LiOH + 25cc of H_2/Kg

Fig.6 Solubility of $Ni_{0.5}$ $Co_{0.05}$ $Fe_{2.45}$ O_4 in 0.06 M H_3BO_3 + 10^{-4}M LiOH + 25cc of H_2/Kg

780 μmolal H$_2$

y-axis: Manganese Concentration mol kg^{-1}
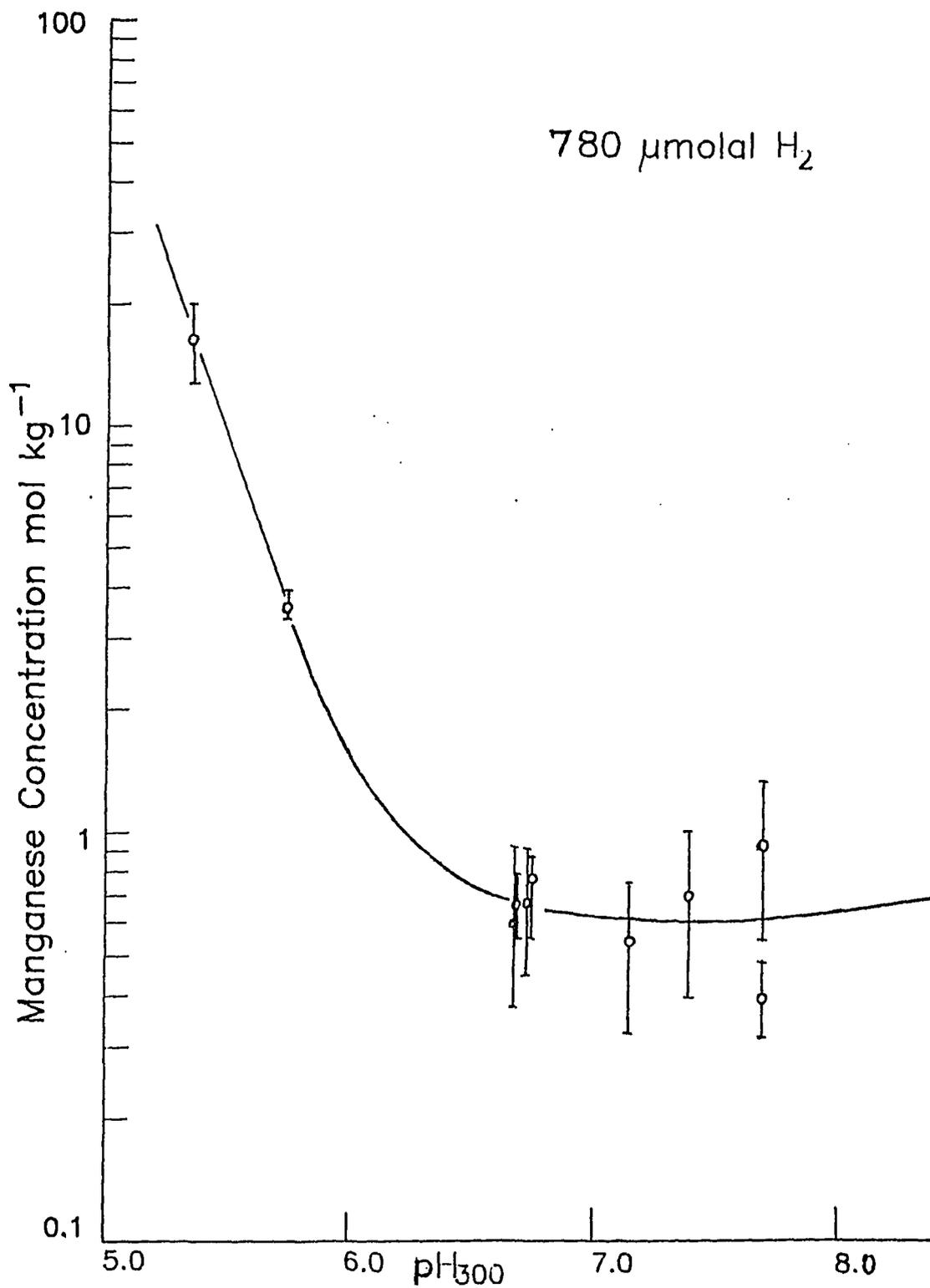
x-axis: pH$_{300}$

Fig.7 Equilibrium Solution Concentration of Manganese from PWR crud at 300 °C