Thermodynamic Evaluation of Nickel Solubility Depending on Redox Environment during Shutdown in PWR Primary Systems

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The solubility of nickel in PWR primary systems during plant shutdown, where pH value and dissolved hydrogen concentrations are decreased, was estimated by taking the redox reactions into calculations, and optimum water chemistry was discussed. The solubility of nickel under reducing condition is limited by equilibrium of Ni^{2+} with nickel metal and decreases with dissolved hydrogen concentration. Under weakly reducing or oxidizing environments, the solubility is limited by precipitation as $NiFe_2O_4$. In order to remove nickel effectively from oxide layers, it is significant to decrease the dissolved hydrogen concentration as low as possible.

1. Introduction

Reduction of occupational radiation exposure to workers during inspection is one of the most important issues in nuclear power industry [1-3].

The main radiation source is ^{58}Co and ^{60}Co which are generated by nuclear reactions; $^{58}Ni(n,p)^{58}Co$ and $^{59}Co(n,\gamma)^{60}Co$ on fuel claddings, respectively. The radioactive cobalt is incorporated into oxide layers on the structural materials during full power operation. It is important to remove the radioactive corrosion products before inspection [1-3].

In primary systems of pressurized water reactor (*PWR*) plants, the double-layered oxides are formed on the nickel based alloy. The outer layer is mainly composed of iron/nickel ferrite and the inner layer contains the iron/nickel chromite. The chromium rich inner layer protects the substrate from corrosion. It is important to preserve the protective inner layer while removing the radioactive corrosion products [1].

In primary systems of *PWR* plants, the *pH* value and the dissolved hydrogen (*DH*) concentrations are decreased during the plant shutdown to remove the radioactive corrosion products before inspection. Oxygen gas and/or hydrogen peroxide are injected to decrease the *DH* concentration and to mitigate the reducing environment. Temperature is controlled approximately 333 *K* [1-5].

However the optimum water chemistry during plant shutdown has not been investigated theoretically. It is important to evaluate the effect of water chemistry such as redox condition or pH on the solubility of nickel.

Thermodynamic solubility of metal has generally been estimated based on the relevant equilibrium constants and charge balance. The solubility can be obtained as functions of temperature and *pH* of high temperature. The solubility also depends on dissolved oxygen (*DO*) and/or *DH* concentrations, which predominantly influence the electrochemical potential. The solubility of nickel in *PWR* primary systems during shutdown was estimated, and optimum water chemistry was discussed.

2. Experimental Methods

Relevant redox reaction depends on oxidant such as *DO*. It is supposed that cathode reaction in the presence of *DH* was supposed to be defined by hydrogen ion reduction ("*redox condition I*", hereinafter). On the other hand, cathode reaction in the presence of *DO* was supposed to be defined by oxygen ion reduction ("*redox condition II*", hereinafter).

The solubility of nickel is also limited by the precipitation as oxides. In PWR primary systems, the main constituent of oxide layer is considered as metal nickel, $NiFe_2O_4$ and/or NiO [1,4]. The solubility of nickel limited by NiO and $NiFe_2O_4$ precipitations were taken into consideration.

The standard Gibbs free energy change and the standard reduction potential of equations used for the calculations are shown in Tables 2 and 3.

2.1. Basic Formulas The solubility of nickel was calculated at 333 K and pH of 5 as a possible condition during plant shutdown.

In aqueous systems, bivalent nickel ion is hydrolyzed. The hydrolysis reaction of bivalent nickel ion is usually considered as shown Eqs. (*a*), (*b*) and (*c*) [7-8]. In the present work, Eqs. (*a*) and (*b*) were taken into account because the formation of $Ni(OH)_3^-$ can be neglected under weakly acidic solutions. The hydrolysis constants of Eqs. (*a*) and (*b*) are given by Eqs. (*1*) and (*2*), respectively.

$$K_a = [NiOH^+] \cdot [H^+]/[Ni^{2+}] \qquad (1)$$

$$K_b = [Ni(OH)_2] \cdot [H^+]^2/[Ni^{2+}] \qquad (2)$$

The solubility of nickel is expressed as a function of equilibrium concentration of Ni^{2+} as shown below.

$$[Ni^{2+}]_T = [Ni^{2+}] + [NiOH^+] + [Ni(OH)_2]$$
$$= [Ni^{2+}](1 + K_a/[H^+] + K_b/[H^+]^2) \qquad (3)$$

The equilibrium concentration of Ni^{2+} is restricted as follows, and the lowest concentration in the three cases determines $[Ni^{2+}]$.
(i) Redox environment defined by Eq. (*d*).
(ii) Precipitation as NiO defined by Eq. (*e*).
(iii) Precipitation as $NiFe_2O_4$ defined by Eq. (*f*).

A hydrolysis constant at 333 K, K_{333} was calcurated using Eq. (*4*) from the standard Gibbs free energy change of the corresponding reaction at 333K, ΔG^o_{333}.

$$K_T = exp(-\Delta G^o(T)/RT) \qquad (4)$$

When a reaction has identical like charges on both sides, the standard Gibbs free energy change can be extrapolated to high temperature using Eq. (*5*) [7,8].

$$\Delta G^o(T) = \Delta G_{298} - \Delta S_{298}(T-298.15)$$
$$+ \Delta C_p\{T-298.15-T \cdot ln(T/298.15)\} \qquad (5)$$

Equations (*4*) and (*5*) results in Eq. (*6*) when the ΔCp can be regarded as 0[8].

$$log\ K = a + b/T \qquad (6)$$

where a and b are constants.

Several equilibrium constants at 333 K can be extrapolated using Eq. (*6*).

2.2. Solubility Limited by Redox Environment
The equilibrium concentration of Ni^{2+} limited by redox environment is estimated from Nernst's equation.
The standard reduction potentials $E_{0,T}$ at 333 K were derived from temperature dependence [9].

The redox reaction and Nernst's equation under the *redox conditions I* and *II* are shown by Eqs. (*g*) or (*7*), and (*h*) or (*8*) respectively.

(i) *Redox condition I*

$$E_g = (E_{Ni2+|Ni}^o - E_{H+|H2}^0)$$
$$- RT/zF \cdot ln\ (a_{H+}^2/a_{Ni2+} \cdot P_{H2}) \qquad (7)$$

(ii) *Redox condition II*

$$E_h = (E_{Ni2+|Ni}^o - E_{O2,H2O,OH-}^0)$$
$$-RT/zF \cdot ln\ (P_{O2}/a_{Ni2+}^2 \cdot a_{OH-}^4) \qquad (8)$$

When Ni^{2+} concentration is low enough, activity coefficient can be regarded as unity, and activity of Ni^{2+} is equal to its concentration. That the equilibrium concentration of Ni^{2+} at a certain potential E depends on the pH and the partial pressure of hydrogen or oxygen. The partial pressure was obtained from the DH and DO concentrations by using Henry's law.

2.3. Solubility Limited by Oxide Precipitation
The equilibrium concentration of Ni^{2+} limited by precipitation as NiO and $NiFe_2O_4$ is shown below.

$$K_e = [H^+]^2/[Ni^{2+}] \qquad (9)$$

$$K_f = [H^+]^8/([Ni^{2+}][Fe^{3+}]^2) \qquad (10)$$

It was considered that redox environment determines stable iron oxide (Fe_3O_4 or Fe_2O_3). In case of *type I* and *III*, Fe_3O_4 is stable. In case of *type II* and *IV*, Fe_2O_3 is stable.
(i) Redox condition I
Type I
Redox environment is defined by Eq. (*i*). Nernst's equation is shown by Eqs. (*11*).

$$E_i=(E_{Fe3+|Fe3O4}^{\ o}-E_{H+|H2}^{\ o})$$
$$-RT/2F \cdot ln(a_{H+}^{\ 18}/a_{Fe3+}^{\ 6} \cdot P_{H2}) \qquad (11)$$

Type II

Redox environment is defined by Eq. (*j*). Nernst's equation is shown by Eqs. (*12*).

$$K_j=[H^+]^6/[Fe^{3+}]^2 \qquad (12).$$

(ii) Redox condition II

Type III

Redox environment is defined by Eq. (*k*). Nernst's equation is shown by Eqs. (*13*).

$$E_k=(E_{Fe3+|Fe3O4}^{\ o}-E_{O2,H+}^{\ o})$$
$$-RT/2F \cdot ln(a_{H+}^{\ 36} \cdot P_{O2}/a_{Fe3+}^{\ 12}) \qquad (13)$$

Type IV

Redox environment is defined by Eq. (*j*). Nernst's equation is shown by Eqs. (*12*).

Stability of Fe_3O_4 and Fe_2O_3 was compared based on the Gibbs free energy as shown below.
(i) Under *redox condition I*, the stability of Fe_3O_4 and Fe_2O_3 is compared by Eq. (*l*).
(ii) Under *redox condition II*, the stability of Fe_3O_4 and Fe_2O_3 is compared by Eq. (*m*)

When Fe_3O_4 is stable, Eqs. (*11*) or (*13*) were used. Otherwise, Eq. (*12*) was used.

Ion product of water at 333 *K* used is shown below [10].

$$K_{w(60°C)}=9.108x10^{-14} \qquad (14)$$

3. Results and Discussion

3.1. Hydrolysis Constants of Nickel Table 1 shows the hydrolysis constants of nickel at 333 *K* [11].

Table 1. Hydrolysis constants of nickel at 333 K.

K_a	1.6×10^{-9} (mol/dm^3)
K_b	1.3×10^{-19} (mol^2/dm^6)

3.2. Solubility limited by redox environment

The solubility of nickel at *pH* 5 was estimated under typical condition during plant shutdown.
3.2.1 *Redox condition I* The equilibrium concentration of Ni^{2+} limited by redox environment was estimated using Eq. (*7*) and temperature dependence of the standard redox potentials.

In reducing conditions, electrochemical potential is determined by *DH* concentration and *pH*.

Equation (*15*) shows the redox potential of hydrogen.

$$E_n= E_{H+|H2}^{\ o} - RT/zF \cdot ln (P_{H2}/a_{H+}^{\ 2}) \qquad (15)$$

From Henry's constant of hydrogen at 333 *K*, P_{H2} was calculated from *DH* concentrations.

The solubility of nickel was derived as a function of *DH*. Figure 1 shows the dependence of the solubility of nickel on the *DH* concentration. Note that the solubility increases with decrease of *DH* concentration.

3.2.2 *Redox condition II* The equilibrium concentration of Ni^{2+} limited by redox environment was estimated using Eq. (*8*).

In oxidizing conditions, electrochemical potential is determined by *DO* concentration and *pH* as shown in Eq. (*16*).

$$E_o=E_{O2,H2O|OH-}^{\ 0} - RT/zF \cdot ln (a_{OH-}^{\ 4}/P_{O2}) \qquad (16)$$

From Henry's constant of oxygen at 333 *K*, P_{O2} was calculated from *DO* concentrations.

The solubility of nickel as a function of *DO* concentration is shown in Fig. 2. Trace *DO* actually oxidizes nickel into Ni^{2+}, and thus the solubility is very high.

3.3 Solubility Limited by Oxide Precipitation

3.3.1 Precipitation of *NiO* The authors calculated nickel solubility limited by precipitation as *NiO*, and compared it with that limited by redox environment. The results are shown in Fig. 3.
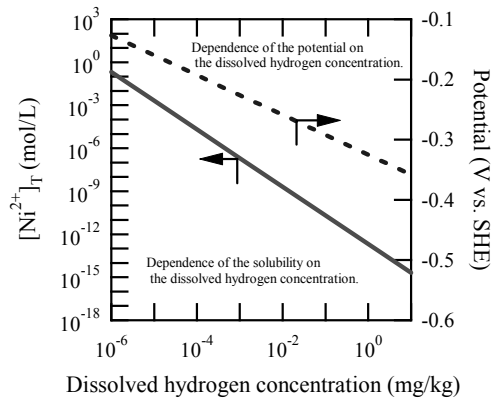

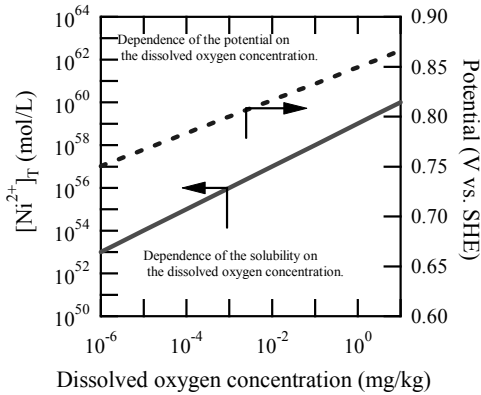Fig 1. Dependence of solubility of nickel on dissolved hydrogen concentration.

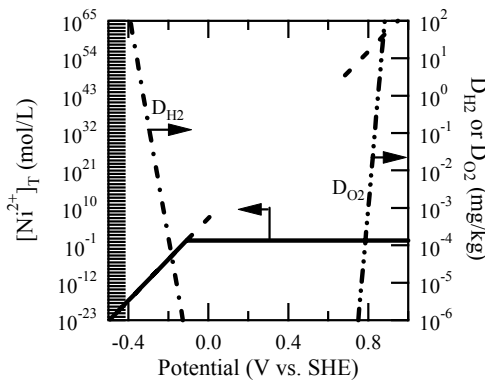Fig 2. Dependence of solubility of nickel on dissolved oxygen concentration.

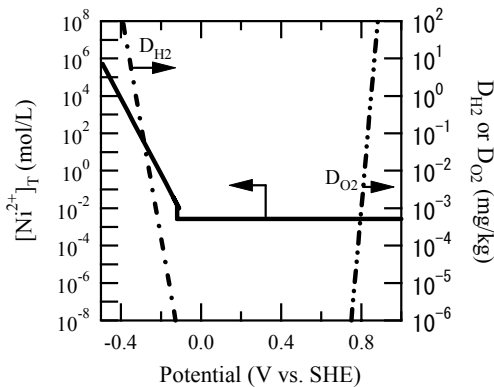Fig 3. Solubility of nickel limited by precipitation of NiO and corrosion of nickel.

Fig 4. Solubility of nickel limited by precipitation of $NiFe_2O_4$.

The nickel solubility was limited by the precipitation of *NiO* over -0.109 *V* (*SHE*) while that was limited by the redox environment below that potential.

3.3.2 Precipitation of *NiFe₂O₃*

The equilibrium concentration of Ni^{2+} limited by the precipitation of $NiFe_2O_4$ at *pH* 5 was derived from Eq. (*10*). The equilibrium concentration of Fe^{3+} was derived from the equilibrium equation with stable iron oxide as shown below.

The threshold *DH* and *DO* concentration of Eqs.(*l*) and (*m*) are 5.61×10^{-7} *mg/kg* and 2.67×10^{-29} *mg/kg*, respectively.

The reaction of *type III* was ignored because the threshold *DO* concentration was considerably low.

Fe^{3+} concentration for *type I* was derived as the function of *DH* concentration from Eq. (*10*).

On the other hand, Fe^{3+} concentration for *type II* and *IV* was calculated from Eq. (*12*). The solubility of nickel was obtained as 2.65×10^{-3} *mol/dm³*.

Figure 4 shows dependence of nickel solubility on electrochemical potential. The solubility of nickel decreases with DH concentration because the equilibrium concentration of Fe^{3+} was increased by oxidation of Fe_3O_4. Under more oxidizing conditions, the equilibrium concentration of Fe^{3+} is determined by equilibrium with Fe_2O_3, and dose not depended on the potential.

The actual solubility of nickel is obtained as the lower value in Figs. 3 and 4. The results are shown in Fig. 5. The solubility of nickel under sufficiently reducing environment was limited by the redox reaction with metal nickel. On the other hand, it was controlled by the precipitation of $NiFe_2O_4$ under slightly reducing or oxidizing environment. A peak of nickel solubility appears in Fig.5. At the peak, nickel metal and $NiFe_2O_4$ are balanced in solid phase.

It is expected from Fig. 5 that $NiFe_2O_4$ in oxide layer can be reduced to nickel metal under sufficiently reducing environment.

3.4 Effect of pH on Nickel Solubility

Figure 6 shows the effect of *pH* on the solubility of nickel at 333 *K*. The solubility of nickel hardly depends on *pH* under sufficiently reducing environment. Contrary, the solubility decreases with increase of *pH* and is independent of potential under slightly reducing or oxidizing environment.

Figure 7 shows the effect of DH on the solubility of nickel at 333 *K*. The solubility of nickel decreases by the increase of pH at constant DH concentration.

It is concluded that the solubility of nickel under oxidizing condition is affected by *pH* rather than *DO* concentration while the solubility of nickel strongly depends on *DH* concentration under reducing condition.

In order to remove effectively nickel from oxide layer, it is significant to decrease *DH* concentration as low as possible. Oxygen gas injection to decrease *DH* concentration should be proceeded attentively without excessive *DO* because the oxidation of metal nickel to *NiFe$_2$O$_4$* is feasible under oxidizing conditions. The target of *DH* concentration should be determined from a view point of protection of structural materials against corrosion.
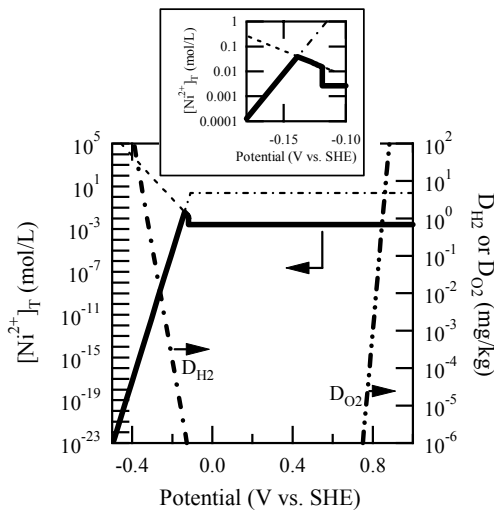
The nickel solubility is increased by decrease of *pH*. However the minimum *pH* should be determined in a similarly way, since low pH generally accelerates corrosion.

4. Conclusions

The solubility of nickel in *PWR* primary system during shutdown was calculated by taking the redox reactions into the calculations. The following conclusions are drawn.

1. The solubility of nickel under reducing condition is limited by equilibrium of *Ni^{2+}* with nickel metal and decreases with increase of *DH* concentration. Under the slightly reducing or oxidizing environment, the solubility is limited by precipitation as *NiFe$_2$O$_4$*.

2. The solubility of nickel under reducing environment hardly depends on *pH*. Under weakly reducing or oxidizing environment, the solubility decreases with increase of *pH*.

3. The solubility of nickel under oxidizing conditions is affected by *pH* rather than *DO* concentrations while it is affected predominantly by *DH* concentration under reducing condition.

4. In order to remove nickel effectively from oxide layer, it is significant to decrease *DH* concentration as low as possible without excessive *DO*.

Fig 5.   Solubility of nickel at 333K under the solution of pH 5.
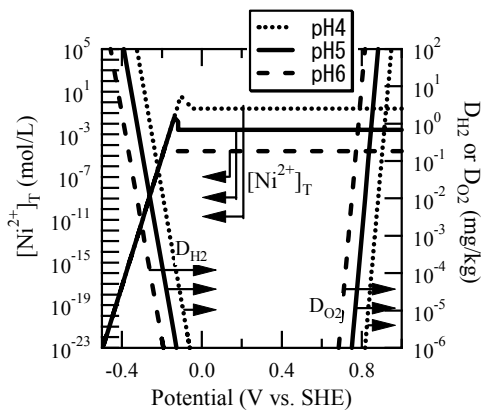
Fig 6.   Effect of pH on solubility of nickel at 333K.
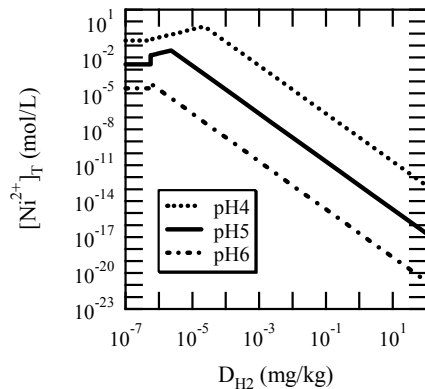

Fig 7.   Effect of dissolved hydrogen on solubility of nickel at 333K.

Table 2. ΔG^o_{298} and ΔG^o_{333} *used for the calculation.*

Eq. No.	Chemical reaction	ΔG^o_{298} (kJ/mol)	ΔG^o_{333} (kJ/mol)	Ref.
(a)	$Ni^{2+} + H_2O$ $= NiOH^+ + H^+$	56.278	56.087	[11]
(b)	$Ni^{2+} + 2 H_2O$ $= Ni(OH)_2 + 2H^+$	119.862	120.384	[11]
(c)	$Ni^{2+} + 3 H_2O$ $= Ni(OH)_3^- + 3H^+$			
(e)	$Ni^{2+} + H_2O$ $= NiO(s) + 2H^+$	69.04	66.190	[12, 13]
(f)	$Ni^{2+} + 2Fe^{3+} + 4H_2O$ $= NiFe_2O_4 + 8H^+$	55.662	36.037	[14, 15]
(j)	$2Fe^{3+} + 3H_2O$ $= Fe_2O_3 + 6H^+$	3.840	-112.899	[11]

Table 3. E^0_{298} and E^0_{333} used for the calculation.

Eq. No.	Chemical reaction	E^0_{298} (V)	E^0_{333} (V)	Ref.
(d)	$Ni(s) = Ni^{2+} + 2e^-$	-0.236	-0.231	[9]
(g)	$Ni^{2+} + H_2 = Ni(s) + 2H^+$	-0.236	-0.231	[9]
(h)	$2Ni^{2+} + 4OH^-$ $= 2Ni(s) + O_2 + 2H_2O$		-0.593	[9, 12]
(i)	$6Fe^{3+} + 8H_2O + H_2$ $= 2Fe_3O_4 + 18H^+$		0.344	[9]
(k)	$12Fe^{3+} + 18H_2O$ $= 4Fe_3O_4 + 36H^+ + O_2$			
(l)	$3Fe_2O_3 + H_2$ $= 2Fe_3O_4 + H_2O$		0.212	[9]
(m)	$6Fe_2O_3 = 4Fe_3O_4 + O_2$		-0.992	[9]
(n)	$2H^+ + 2e^- = H_2$	0	0	[9]
(o)	$O_2 + 2H_2O + 4e^- = 4OH^-$	0.4011	0.342	[9]

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