Res. Rep. Fac. Eng. Mie Univ., Vol. 18, pp. 49-58 (1993)

Original Paper

Statistical Comparison of Iron Solubility of Magnetite and Nickel Ferrites

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(Received September 16, 1993)

Solubility of nickel ferrites and magnetite was studied the thermodynamically and from the standpoint of dissolution and precipitation reactions at equilibrium. The results suggest that nickel ferrite dissolves to form nickel ion and ferrous ion, and ferrous ion precipitates to form magnetite :

$$NiFe_2O_4 + 6H^+ + H_2 \rightarrow Ni^{2+} + 2Fe^{2+} + 4H_2O$$
$$\rightarrow 3Ni^{2+} + Fe_3O_4 + 12H^+ + 2H_2$$
$$\rightarrow 3Fe^{2+} + 4H_2O$$

Statistical analysis of solubility data from the literatures indicated that the difference in the solubility of ferrous species between nickel ferrite and magnetite was not significant. From these considerations it is conceivable that the solubility of ferrous species from nickel ferrite is the same as that from magnetite.

Key words : Solubility, Nickel ferrite, Magnetite, High-temperature.

1. INTRODUCTION

Radioactive occupational exposure of workers and treatment/disposal of radioactive wastes are major problems in nuclear power plant operation. Many endeavors have been made to reduce radioactivation of corrosion products(CP) and accumulation of radioactive CP. many recent research projects have been carried out in this area by improving the pH control range of primary coolant in Pressurized Water Reactor. In order to estimate theoretically the optimized pH range in which the solubility is a minimum and nearly independent of temperature in the range from 285℃ to 320 ℃, it is essential to obtain precise data of the solubility of cobalt and/or nickel ferrite and their temperature dependency. The solubility of nickel ferrites was reported as a funcion of temperature by several researchers[1)-6)] . The reported data, however, show large scatter, and further the term "solubility of compound oxides" such as nickel ferrite($NiFe_2O_4$) is ambiguously used, because there may be several reactions at equilibrium.

This paper discusses the dissolution and precipitation equilibrium of the ferrites thermodynamically, focusing on the iron component. The derived equilibrium reactions were verified by statistical analysis of the reported solubility data of $NiFe_2O_4$ and magnetite(Fe_3O_4) and evaluation of the solubility difference of the iron component between them.

2. Solubility - Dissolution and Precipitation Equilibrium

Solubility is the concentration of dissolved species in a saturated solution, in which dissolution of a solid compuond and precipitation of dissolved species are in balance. Generally speaking, dissolution and precipitation are the same reaction, and are in equilibrium. In the case of $NiFe_2O_4$, however, the equilibrium reactions are complicated. The dissolution reaction proceeds to the left in the reaction :

$$NiFe_2O_4 + 6H^+ + H_2 = Ni^{2+} + 2Fe^{2+} + 4H_2O \qquad (1)$$

but the precipitation reaction does not necessarily proceed to the right, since Ni^{2+} and Fe^{2+} can behave independently in the solution. Ni^{2+} and Fe^{2+} could produce NiO or Fe_3O_4 separately, and $NiFe_2O_4$ combinedly as a precipitate, depending on the solubility of these products. An oxide with minimum solubility should precipitate first. Hence three cases are postulated :

1) $NiFe_2O_4$ has a minimum solubility. In this case the solubility equilibrium should be expressed by reaction (1)

2) Fe_3O_4 has a minimum solubility and precipitates first. The solubility equilibrium of Fe^{2+} should be as follows:

$$3Fe^{2+} + 4H_2O = Fe_3O_4 + 6H^+ + H_2 \qquad (2)$$

Hence the equilibrium concentration of Fe^{2+} for $NiFe_2O_4$ is the same for Fe_3O_4. On the other hand, the solubility of the Ni^{2+} component is determined by the equilibrium of the reaction (1), presuming that the Fe^{2+} concentration is determined by the reaction (2).

3) NiO has a minimum solubility and precipitates first. The solubility equilibrium of Ni^{2+} should be as follows:

$$Ni^{2+} + H_2O = NiO + 2H^+ \qquad (3)$$

Hence the equilibrium concentration of Ni^{2+} for $NiFe_2O_4$ is the same for NiO. On the other hand, the solubility of the Fe^{2+} component is determined by the equilibrium of the reaction (1), presuming that the Ni^{2+} concentration is determined by the reaction (2)

3. THERMODYNAMIC CONSIDERATIONS

In order to predict the reaction direction of dissolution and precipitation , Gibbs energy changes were calculated for the dissolution reaction of nickel ferrite and magnetite, and the precipitation reactions of nickel ion and ferrous species at 300 ℃. Table 1 shows standard Bibbs energies of formation of constituent species, which were selected to be the most correct of the reported values[7)8)]. Using the data in Table 1, the Bibbs energy changes of dissolution and precipitation reactions were calculated and are shown in Table 2. These values indicated that the dissolution reactions of $NiFe_2O_4$(1) and Fe_3O_4(4) have negative Bibbs energy changes, and can proceed naturally. Eventually, for the reverse precipitation reactions the changes are positive and the reactions should proceed only to the saturation condition of the ion species. It is worth noting that the dissolution reaction forming Ni^{2+} and Fe_3O_4 has a negative Bibbs energy change, and could proceed naturally. This suggests nickel species dissolve preferentially and Ni^{2+} can be held in solution in the presence of Fe_3O_4 which dissolves according to the reaction(2). From this discussion it is considered that the solubility equilibrium of nickel ferrite isestablished preferentially according to case 2) mentioned above.

Table 1. Standard Free Energies of Formation Used for the Calculation at 300 ℃

Ion or Compound	Standard Gibbs Energy of Formation kcal/mole	Literature
Ni^{2+}	1.073	6)
Fe^{2+}	21.807	6)
Fe_3O_4	220.652	6)
H_2O	46.701	6)
NiO	44.577	6)
$NiFe_2O_4$	209.256	7)

Table 2. Free Energy Change for the Dissolution Reactions and the Precipitation Reactions at 300 ℃

Reactions	Standard Gibbs Energy Change (kcal/mol)
1) $NiFe_2O_4 + 6H^+ + H_2 \rightarrow Ni^{2+} + 2Fe^{2+} + 4H_2O$	− 22.2
2) $Ni^{2+} + 2Fe^{2+} + 4H_2O \rightarrow NiFe_2O_4 + 6H^+ + H_2$	+ 22.2
3) $3Fe^{2+} + 4H_2O \rightarrow Fe_3O_4 + 6H^+ + H_2$	+ 31.6
4) $Fe_3O_4 + 6H^+ + H_2 \rightarrow 3Fe^{2+} + 4H_2O$	− 31.6
5) $Ni^{2+} + H_2O \rightarrow NiO + 2H^+$	+ 3.2
6) $3NiFe_2O_4 + 6H^+ + H_2 \rightarrow 3Ni^{2+} + 2Fe_3O_4 + 4H_2O$	− 3.5

4. ANALYSIS OF REPORTED DATA

In order to verify the validity of the above-mentioned considerations, that is, the iron solubility of nickel ferrite and magnetite should be equal, we analyzed the reported solubility data of $NiFe_2O_4$ and Fe_3O_4 statistically. The solubility of $NiFe_2O_4$ and Fe_3O_4 has been reported by Kunig and Sandler[3)] and by Lambert[4)] in a solution containing 0.06M $B(OH)^3$, 1.0 X 10^{-4}M LiOH and, 25 cm^3 H_2/kgH_2O and 17 cm^3 H_2/kg

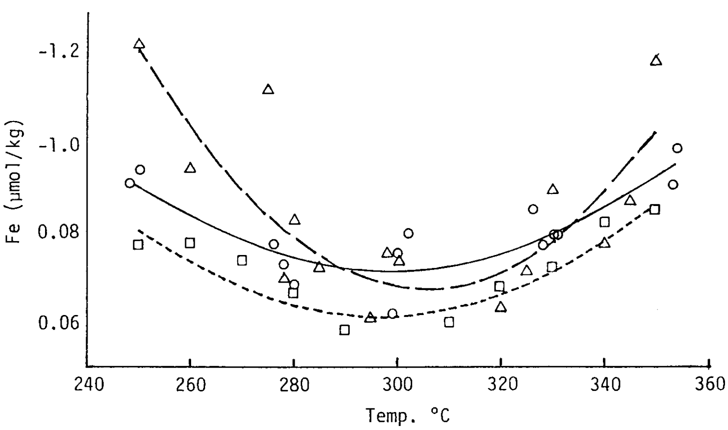

Figure 1. Comparison of Iron Solubility from Magnetite and Nickel Ferrites. Data of Lambert[4)5)]

H_2O, respectively. Mitsubishi Heavy Industry[5] also measured the solubility of $NiFe_2O_4$ in the solution containing 0.043 MB(OH)^3, 1.3 X 10^{-4}M LiOH and 17cm^3 H_2/kg H_2O. These data differed considably from each other, As shown in Figure 1. Hence using the data measured by the same researcher, the comparison of the solubility of iron species was made between nickel ferrite and magnetite.

Plotting Lambert's data[4], including a series of magnetite and two series of a nickel ferrite, against temperature, the curves of parabolic form were obtained for each series. When the data were divided into two groups for the temperature t, $t < 300$ ℃ and $t > 300$ ℃, and logarithms of iron solubilities were plotted against temperature, linear relationships were obtained as shown in Figure 2 and 3. Using these relationships simplifies the statistical analysis.

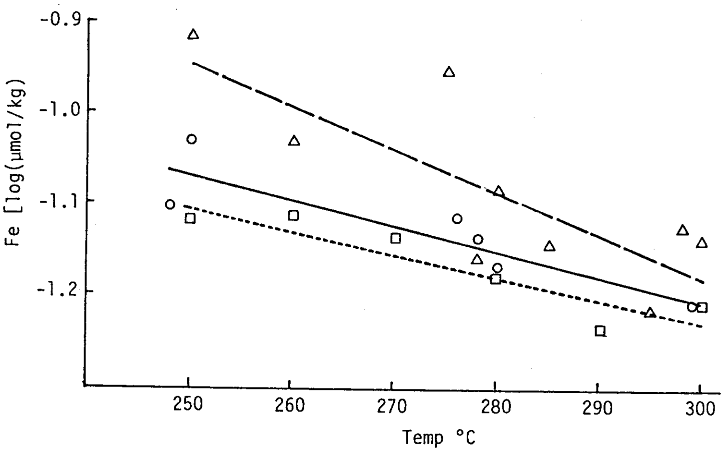

Figure 2. Plot of Logarithmus of Iron Solubility against Teperature. ≦ 300℃
Data of Lambert[4)5)]
○ : Magnetite, △,□ : Each Series of Nickel

For $t < 300$ ℃, the curve of magnetite was in the middle of those of the two nickel ferrite series. At $t > 300$ ℃, a similar tendency was obtained in the range from 300 ℃ to 335 ℃.

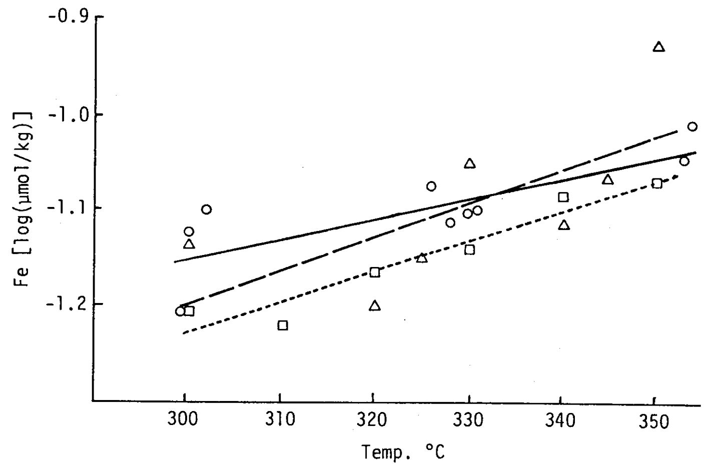

Figure 3. Plot of Logarithmus of Iron Solubility against Teperature. ≧ 300℃
Data of Lambert[4)5)]
○ : Magnetite, △,□ : Each Series of Nickel

Kunig and Sandler[3] reported extensive data on the solubility of iron and nickel from nickel ferrites over a wide temperature range, but magnetite only in a restricted temperature range. Then their solubilities have been compared only in a temperature range from 250 to 305℃, as shown in Figure 4. They used various nickel ferrites such as $Ni_{0.75}Fe_{2.25}O_4$, $Ni_{0.95}Fe_{2.05}O_4$, $Ni_{0.35}Fe_{2.65}O_4$, $Ni_{0.50}Co_{0.05}Fe_{2.45}O_4$. Although the iron contents in these ferrites are different, they are combined and analysed as a ferrite, because the difference in the solubilities of the iron spec-ies were considered to be within the experimental scatter.

Statistical regression and variance analysis were performed for each case and the results are shown in the appendix(Table A-1 to A-8).

5. F-TEST

The F-test was applied to statistically determine whether or not the difference in the solubility regression curves between $NiFe_2O_4$ and Fe_3O_4 is significant. At first the sum of squares of residuals of linear regression was calculated for magnetite (RSS_1) and nickel ferrite (RSS_2) individually, and for the two in a lump (RSS_0). Then the statistic (W^{obs}) for the F-test was calculated:

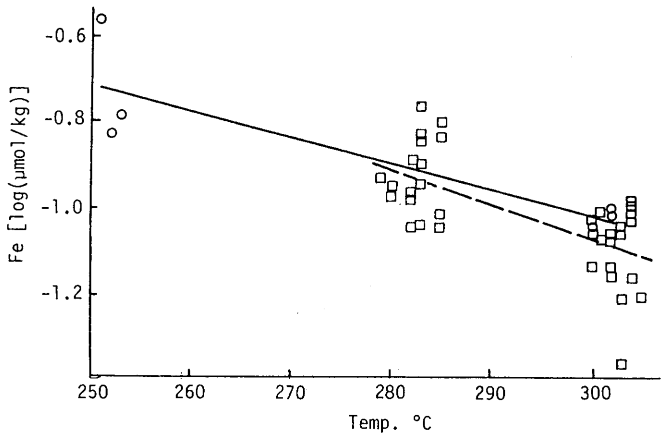

Figure 4. Plot of Logarithmus of Iron Solubility against Teperature.
≧ 300℃ Data of Kunig[3)]
○ : Magnetite,
△, □ : Each Series of Nickel

$$W^{obs} = [(RSS_0 - RSS)/RSS] \div [p/(n-2p)] \qquad (4)$$

where $RSS = RSS_1 + RSS_2$. The values of WObs is compared with the corresponding values for the F-distribution; if the former is larger than the latter, the difference in the solubility is not significant.

As shown in Table 3, at confidence limits of 99% no difference was found in the solubility between magnetite and nickel ferrites, and at confidence limits of 95% there was also no difference except in three cases:

Table 3 F-test for difference in solubility between magnetite and nickel ferrites

	Lambert's data						Kunig Sandle data
	t < 300 ℃			t > 300 ℃			
	a series	another	both	a series	another	both	
RSS_1(magnetite)	.00407			0.0790			0.0398
RSS_2($NiFe_2O_4$)	0.0295	0.0023	0.0708	0.0251	0.0014	0.0375	0.303
RSS_0	0.0593	0.0092	0.0786	0.0354	0.0202	0.0474	0.405
W^{obs}	4.15	0.011	0.42	0.44	6.4	0.44	3.7
F-value C.L. 95 %	3.98	4.46	3.59	3.88	3.98	3.49	3.23
99 %	7.20				7.20		5.17
Test of significance 95 %	YES	NO	NO	NO	YES	NO	YES
99 %	NO				NO		NO
difference in solubility	NO	NO	NO	NO	NO	NO	NO

1) Lambert's data, t ≦ 300℃, the test for a series of nickel ferrite,
2) Lambert's data, t ≦ 300℃, the test for another series of nickel ferrite,
3) Kunig and Sandler's data, for which the difference was significant. The results are considered to give substantial evidence in support of the thermodynamic-

al consideration mentioned above.

6. Summary

The thermodynamical consideration of the solubility reactions indicated nickel ferrite dissolved to form nickel ion and ferrous species under the following solubility equilibrium :

$$NiFe_2O_4 + 6H^+ + H_2 \rightarrow Ni^{2+} + 2Fe^{2+} + 4H_2O \rightarrow 3Ni^{2+} + Fe_3O_4 + 12H^+ + 2H_2 \rightarrow 3Fe^{2+} + 4H_2O$$

The statistcal analysis of the reported solubility data indicated that there are no significant differences in the solubility of ferrous species between nickel ferrite and magnetite.

Conclusively it is conceivable that the solubility of iron species from nickel ferrite is the same as that of magnetite.

ACKNOWLEDGEMENT

We thank Prof. Toshiro Haga for helpful advice about statistical analysis and the members of the National Committee for WG-B in Japan National Committee of IAPWS for valuable discussion and comments.

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Appendix

Table A-1. Analysis of Variance—Linear Regression by Least Squares—
Regression Line : $\log S_{Fe} = A_0 + A_1T + A_2T^2$
Solubility Data of Lambert[4)]

Oxides	Constant	Value	Standard Error	t-Statistic Value
Fe_3O_4	A_0	0.762	0.116	6.56
	A_1	-0.00463	0.000776	-5.69
	A_2	0.05776	1.29	6.04
	n = 14, R_2 = 0.775, s = 0.00510			
Nickel Ferrite -1	A_0	1.689	0.343	4.9292
	A_1	-0.0106	0.00228	-4.6565
	A_2	0.04174	3.76	4.6262
	n = 15, R_2 = 0.648, s = 0.0123			
Nickel Ferrite -2	A_0	0.818	0.114	7.20
	A_1	-0.00510	0.03763	-6.68
	A_2	0.05860	1.27	6.77
	n = 11, R_2 = 0.859, s = 0.00372			

Table A-2. Analysis of Variance—Linear Regression by Least Squares—
Regression Line : $\log S_{Fe} = A_0 + A_1T$
$\leq$300 ℃. Solubility of Data of Lambert[4)]

Oxides	Constant	Value	Standard Error	t-Statistic Value
Fe_3O_4	A_0	-0.393	0.199	-1.97
	A_1	-0.00267	0.000731	-3.69
	n = 7, R_2 = 0.773, s = 0.0319			
Nickel Ferrite (2 Series)	A_0	-0.219	0.319	-0.685
	A_1	-0.00323	0.00115	-2.82
	n = 15, R_2 = 0.380, s = 0.0738			
Fe_3O_4 + Nickel Ferrite	A_0	-0.307	0.226	-1.36
	A_1	-0.00294	0.03816	-3.61
	n = 21, R_2 = 0.407, s = 0.0643			

Table A-3. Analysis of Variance—Linear Regression by Least Squares—
Regression Line : $\log S_{Fe} = A_0 + A_1T$
≧300 ℃. Solubility of Data of Lambert[4]

Oxides	Constant	Value	Standard Error	t-Statistic Value
Fe_3O_4	A_0 A_1	-1.798 0.00215	0.184 0.03565	-9.77 3.81
	n = 8, R_2 = 0.674, s = 0.0336			
Nickel Ferrite (2 Series)	A_0 A_1	-2.279 0.00354	0.295 0.03898	-7.74 3.95
	n = 15, R_2 = 0.586, s = 0.0537			
Fe_3O_4 + Nickel Ferrite	A_0 A_1	-2.022 0.00279	0.188 0.03576	-10.74 4.85
	n = 21, R_2 = 0.540, s = 0.0487			

Table A-4. Analysis of Variance-Linear Regression by Least
Squares-Regression Line : $\log S_{Fe} = A_0 + A_1T$
≦300 ℃. One Series of Lambert[4]

Oxides	Constant	Value	Standard Error	t-Statistic Value
Fe_3O_4	A_0 A_1	-0.393 -0.00267	0.199 0.000731	-1.97 -3.69
	n = 6, R_2 = 0.773, s = 0.0319			
Nickel Ferrite (1 Series)	A_0 A_1	0.203 -0.00460	0.380 0.00135	0.536 -3.40
	n = 9, R_2 = 0.623, s = 0.0649			
Fe_3O_4 + Nickel Ferrite	A_0 A_1	-0.201 -0.00326	0.271 0.0398	-0.742 -3.34
	n = 15, R_2 = 0.461, s = 0.0651			

Table A-5. Analysis of Variance-Linear Regression by Least Squares-Regression Line : $\log S_{Fe} = A_0 + A_1T$ $\leqq 300$ ℃. Another Series of Lambert[4)]

Oxides	Constant	Value	Standard Error	t-Statistic Value
Fe_3O_4	A_0 A_1	-0.393 -0.00267	0.199 0.000731	-1.97 -3.69
	$n = 6$, $R_2 = 0.773$, $s = 0.0319$			
Nickel Ferrite (Another Series)	A_0 A_1	-0.492 -0.00245	0.157 0.0357	-3.14 -4.31
	$n = 6$, $R_2 = 0.823$, $s = 0.0238$			
Fe_3O_4 + Nickel Ferrite	A_0 A_1	-0.420 -0.00266	0.137 0.03499	-3.07 -5.33
	$n = 12$, $R_2 = 0.740$, $s = 0.0303$			

Table A-6. Analysis of Variance-Linear Regression by Least Squares-Regression Line : $\log S_{Fe} = A_0 + A_1T$ $\geqq 300$ ℃. One Series of Lambert[4)]

Oxides	Constant	Value	Standard Error	t-Statistic Value
Fe_3O_4	A_0 A_1	-1.80 0.00215	0.184 0.03565	-9.77 3.81
	$n = 9$, $R_2 = 0.674$, $s = 0.0336$			
Nickel Ferrite (1 Series)	A_0 A_1	-2.26 0.00353	0.560 0.00169	-4.03 2.08
	$n = 7$, $R_2 = 0.465$, $s = 0.0709$			
Fe_3O_4 + Nickel Ferrite	A_0 A_1	-1.94 0.00258	0.225 0.0369	-8.64 -3.76
	$n = 16$, $R_2 = 0.503$, $s = 0.0503$			

Table A-7. Analysis of Variance-Linear Regression by Least Squares-Regression Line : $\log S_{Fe} = A_0 + A_1 T$ ≥ 300 ℃. Another Series of Lambert[4]

Oxides	Constant	Value	Standard Error	t-Statistic Value
Fe_3O_4	A_0	-1.80	0.184	-9.77
	A_1	0.00215	0.0357	3.81
	$n = 9$, $R_2 = 0.674$, $s = 0.0336$			
Nickel Ferrite (1 Series)	A_0	-2.19	0.145	-15.0
	A_1	0.00319	0.03447	7.14
	$n = 6$, $R_2 = 0.927$, $s = 0.0187$			
Fe_3O_4 + Nickel Ferrite	A_0	-1.93	0.177	-10.9
	A_1	0.00249	0.03543	4.59
	$n = 15$, $R_2 = 0.618$, $s = 0.0394$			

Table A-8. Analysis of Variance-Linear Regression by Least Squares-Regression Line : $\log S_{Fe} = A_0 + A_1 T$ ≤ 300 ℃. Kunig Data[5]

Oxides	Constant	Value	Standard Error	t-Statistic Value
Fe_3O_4	A_0	0.808	0.458	1.76
	A_1	-0.00608	0.00165	-3.69
	$n = 6$, $R_2 = 0.773$, $s = 0.0997$			
Nickel Ferrite* (4 Series)	A_0	1.401	0.425	3.29
	A_1	-0.00825	0.00145	-5.69
	$n = 39$, $R_2 = 0.467$, $s = 0.0905$			
Fe_3O_4 + Nickel Ferrite*	A_0	1.164	0.279	4.18
	A_1	-0.00743	0.03970	-7.77
	$n = 45$, $R_2 = 0.584$, $s = 0.0907$			

* : Nickel Cobalt Ferrite is included.