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APPENDICES

Appendix A Calculation of Nickel Ferrite Composition from EDX

Data given by EDX were the weight percentage of iron as iron oxide (FeO) and of nickel as nickel oxide (NiO). The molecular weights of iron oxide and nickel oxide are 71.84 and 74.71, respectively, and the total atom of nickel and iron has to be three in order to form $Ni_xFe_{3-x}O_4$. Hence, one can calculate the composition of the nickel ferrite, which was found to be $Ni_{0.72}Fe_{2.28}O_4$. The summarized calculations are shown in Table A1.

Table A1 Summary of composition calculation

Sample number	Weight %		
	FeO	NiO	
1	68.13	22.24	
2	67.04	22.61	
3	67.68	21.61	
Average	67.62	22.15	
Mole	0.941	0.296	Total mole of Fe and Ni = 1.237
Composition	$0.941 \times 3 / 1.237$ = 2.28	$0.296 \times 3 / 1.237$ = 0.72	

Appendix B Calculation of Nickel Ferrite Lattice Parameter

An interplanar spacing, d , can be calculated by Bragg's law

$$n\lambda = 2d \sin \theta \quad (\text{B1})$$

when n is usually unity, and λ is an x-ray wavelength, in this case 1.5406 Å. Since the crystal structures of both nickel ferrite and magnetite are cubic, the lattice parameter, a_0 , can be calculated by

$$a_0 = d\sqrt{h^2 + k^2 + l^2} \quad (\text{B2})$$

where h, k, l are planar indices corresponded to each peak.

Table B1 shows the lattice parameters calculated from major peaks; peaks with very low intensity were neglected. According to error statistics, the lattice parameter calculated from the highest degree with reasonable intensity (around 62.9° in this case) is chosen to be the most accurate value of the substance (Cullity, 1978).

Table B1 Lattice parameter values of each peak from XRD analysis

Position of peak, 2θ (degree)	h	k	l	d (Å)	a_0 (Å)
18.4	1	1	1	4.81920	8.347
30.26	2	2	0	2.95199	8.350
35.64	3	1	1	2.51775	8.350
37.28	2	2	2	2.41067	8.350
43.32	4	0	0	2.08752	8.350
53.76	4	2	2	1.70418	8.349
57.32	5	1	1	1.60651	8.348
62.94	4	4	0	1.47591	8.349

Appendix C XRD Pattern of a Bare Zirconium Surface

A bare zirconium surface was analyzed with XRD to identify zirconium peaks, as shown in Figure C1. Such peaks were then used to distinguish nickel ferrite peaks in the XRD pattern obtained from the coupons with their deposits.

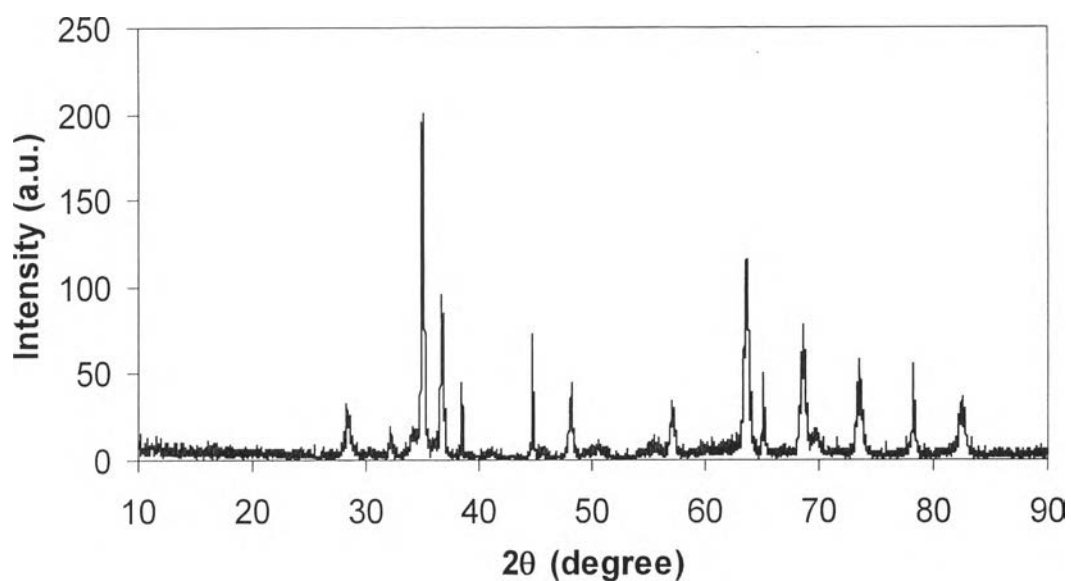


Figure C1 XRD pattern of a bare zirconium surface.

Appendix D Boron Concentration Determination

Boron concentration from boric acid can be determined by titration (Irvine, 1970; EPRI NP-7077, 1990). Boric acid alone cannot be titrated to a precise volumetric endpoint because it is a weak acid. However, the addition of certain polyhydroxyl organic compounds to boric acid solutions results in the formation of complex acids with boric acid, which then can be titrated. In this work, mannitol was used as polyhydroxyl organic compound, and the procedure was as follows.

Sodium hydroxide solution of 0.0265 M was standardized with oxalic acid solution, the primary standard solution. The preparation and standardization of sodium hydroxide are described in general chemistry books. Ten ml of boric acid solution was pipetted in 250-ml Erlenmeyer flask. Three grams of mannitol were added, together with 10 ml of de-ionized water and three drops of phenolphthalein, into the flask. The solution was swirled well, and kept swirling as sodium hydroxide solution was added during the titration. The titration reached endpoint when the solution turned pink. In a sample, two titrations were required. The reaction between sodium hydroxide and boric acid is one to one mole ratio. Here is the example of calculation for boron concentration.

Concentration of NaOH 0.0265 M

Volume of NaOH used 40 ml

Volume of boric acid sample solution 10 ml

Hence, concentration of boric acid in the solution = $0.0265 \times 40 / 10 = 0.106$ M

Molecular weights of boric and boron are 61.8 and 10.8, respectively.

Therefore, 0.106 M of boric acid = $0.106 \times 61.8 \times 10.8 / 61.8 \times 1000 = 1145$ ppm B

Appendix E Deposit Thickness and Deposition Velocity Calculations

Deposited particles were removed from the coupons and dissolved in acid solution. The concentrations of iron and nickel were then determined with ICP-OES and calculated to the amounts per coupon areas. Since the characterization showed that the deposits were mainly composed of injected nickel ferrite, $\text{Ni}_{0.72}\text{Fe}_{2.28}\text{O}_4$, the amounts of iron and nickel were converted to the amount of nickel ferrite. Deposit thickness was estimated by assuming a crud density of 2 g/cm^3 . Deposition velocity was calculated from the concentration of injected nickel ferrite, 500 ppb, and the duration of the experiment. Example of calculation is shown in Table E1.

Table E1 Calculations of deposit thickness and deposition velocity from Run1

Iron concentration (ppm)	36.40
Nickel concentration (ppm)	3.50
Sample volume (ml)	100
Coupon area (cm^2)	3.577
Amount of Fe (mg/cm^2)	$= 36.40 \times 100 / 3.577 / 1000 = 1.018$
Amount of Ni (mg/cm^2)	$= 3.50 \times 100 / 3.577 / 1000 = 0.376$
Amount of nickel ferrite based on Fe (mg/cm^2)	$= 1.018 \times 233.59 / 127.32 = 1.867$
Amount of nickel ferrite based on Ni (mg/cm^2)	$= 0.376 \times 233.59 / 42.27 = 2.078$
Amount of nickel ferrite based on average (mg/cm^2)	$= (1.867 + 2.078) / 2 = 1.972$
Deposit thickness (μm)	$= 1.972 \times 10 / 2 = 9.86$
Deposition velocity (cm/h)	$= 1.972 \times 1000 / 140 / 0.5 = 28.17$

Appendix F Calculation of the Change in Boron Concentration Due to Water Evaporation

At the end of each experiment, the autoclave was isolated, and the samples were taken at various times. Boron concentrations in each sample might not be the same since the water in the autoclave would evaporate to compensate the volume loss due to the sampling. Calculation is required to observe the change in boron concentration due to water evaporation. Temperature was recorded, saturated condition was assumed during the sampling, and thirty milliliters of samples were taken each time. Based on mass balance, one can calculate the boron concentration. Table F1 summarizes the calculation of the boron hideout return result from Run1.

Table F1 Calculation of the change in boron concentration due to evaporation

Time (min)	0	5	10	30	60	180
Temperature (°C)	296	269	253	202	152	93
Density of liquid water (kg/m ³)	720.47	769.46	794.80	862.34	915.13	963.20
Density of water vapor (kg/m ³)	43.178	27.584	21.009	8.174	2.677	0.471
Water left in the autoclave (kg)	0.683	0.653	0.623	0.593	0.563	0.533
Liquid water left in the autoclave (kg)	0.681	0.649	0.618	0.590	0.562	0.533
Amount of boron left in the autoclave (mg)	712.600	681.100	649.584	618.174	586.846	555.563
Calculated boron concentration (ppm)	1047	1050	1051	1047	1044	1043

Appendix G Radiation Statistical Analysis

Poisson statistics is applied in radiation counting (Knoll, 1989; Tsoufanidis, 1995; and Hussein, 2003). Therefore, the variance, σ^2 , of any measurement is equal to its count, C .

$$\sigma^2 = C \quad (\text{G1})$$

Then standard deviation is equal to σ .

The calculation of error in the ratio of the counts with and without boric acid, ε_R , is based on propagation of errors as follows:

$$R = \frac{\bar{C}_0}{\bar{C}_b} \quad (\text{G2})$$

$$\sigma_R^2 = \bar{\sigma}_0^2 \left(\frac{\partial R}{\partial \bar{C}_0} \right)^2 + \bar{\sigma}_b^2 \left(\frac{\partial R}{\partial \bar{C}_b} \right)^2 \quad (\text{G3})$$

$$\sigma_R^2 = \frac{\bar{C}_0}{m} \left(\frac{1}{\bar{C}_b} \right)^2 + \frac{\bar{C}_b}{m} \left(\frac{\bar{C}_0}{\bar{C}_b^2} \right)^2 \quad (\text{G4})$$

$$\varepsilon_R = \sigma_R = \sqrt{\frac{\bar{C}_0}{m\bar{C}_b^2} + \frac{\bar{C}_0^2}{m\bar{C}_b^3}} \quad (\text{G5})$$

where R is the count ratio of counts with and without boric acid.

In order to distinguish the presence of boron, the counts with and without any boron should not differ by at least 2σ for 95% confident level. That is

$$\bar{C}_0 - \bar{C}_{b,\min} \geq 2\bar{\sigma}_0 + 2\bar{\sigma}_b \quad (\text{G6})$$

Since the ratio between with and without boron is obtained from experiments, the equation can be arranged finally to

$$\bar{C}_{b,\min} \geq \left[\frac{2\sqrt{R} + 1}{R - 1} \right]^2 \quad (\text{G7})$$

\bar{C}_b calculated from Eq. (G7) is the minimum count that should be obtained in order to claim that one can distinguish the presence of boron. One can increase the count to be higher than minimum by using a stronger source or increasing the counting period. In addition, improving the ratio, R , can reduce $\bar{C}_{b,\min}$.

Appendix H Calculation of Total Interaction Rate

Total interaction rate can be expressed by $\Sigma\phi V$, where

$$\Sigma = \sum_i N_i \sigma_i = \text{macroscopic cross section}$$

ϕ = neutron flux

V = volume of substance

$$N_i = \frac{w_i \rho}{A_i u} = \text{atomic density of substance } i$$

σ_i = microscopic cross section of substance i

w_i = weight fraction of substance i

ρ = density

A = atomic weight

u = atomic mass unit = 1.66×10^{-27} kg

Properties of elements used for calculation are summarized in Table C1. The autoclave used in this experiment was Hastelloy C, which contains Ni about 50% by weight. The inside diameter and the thickness were 114 mm and 6 mm, respectively. Boric acid powder, H_3BO_3 , was contained in a tube with 11 mm inside diameter.

For boron, $\Sigma_B = N_{B-10} \sigma_{B-10} + N_{B-11} \sigma_{B-11}$

$$\begin{aligned} &= \frac{w_{B-10} \rho}{10 \times u} \sigma_{B-10} + \frac{w_{B-11} \rho}{11 \times u} \sigma_{B-11} \\ &= \frac{0.183 \times 2340 \times 3837 \times 10^{-28}}{10 \times 1.66 \times 10^{-27}} + \frac{0.817 \times 2340 \times 0.005 \times 10^{-28}}{11 \times 1.66 \times 10^{-27}} \\ &= 9898 \text{ m}^{-1} \end{aligned}$$

Boron is present in the form of boric acid. Therefore, weight fraction of boron must be taken into account.

$$\text{Weight fraction of boron in boric acid} = \frac{10.8}{3 + 10.8 + 48} = 0.175$$

$$\begin{aligned}
\text{For nickel, } \sum_{Ni} &= N_{Ni-58} \sigma_{Ni-58} + N_{Ni-60} \sigma_{Ni-60} \\
&= \frac{0.715 \times 8900 \times 4.503 \times 10^{-28}}{58 \times 1.66 \times 10^{-27}} + \frac{0.285 \times 8900 \times 2.9 \times 10^{-28}}{60 \times 1.66 \times 10^{-27}} \\
&= 37.15 \text{ m}^{-1}
\end{aligned}$$

Nickel in Hastelloy C is about 50%.

Ratio of total interaction rate between boron and nickel was calculated by assuming that the autoclave and boric acid powder were exposed to the same amount of neutron flux.

$$\text{Ratio of total interaction rate} = \frac{0.175 \sum_B V_B}{0.5 \sum_{Ni} V_{Ni}} = \frac{0.175 \sum_B \pi D_B^2 h / 4}{0.5 \sum_{Ni} \pi D_{Ni} h t}$$

where D_B , D_{Ni} are diameter of the tube and the autoclave, respectively, h is the height of the autoclave and boric acid powder, and t is the autoclave thickness. Substitute all numbers, and one can obtain

$$\text{Ratio of total interaction rate} = \frac{0.175 \times 9898 \times 1.1^2 / 4}{0.5 \times 37.15 \times 11.4 \times 0.6} = 4.12$$

It can be concluded that boron interacts with neutrons and produces about four times as many photons as nickel.

Table H1 Nuclear properties of boron and nickel

Element	Boron	Nickel
Density (kg/m ³)	2340	8900
Natural isotopes (weight fraction)	B-10 (0.183) B-11 (0.817)	Ni-58 (0.715) Ni-60 (0.285)
Radiative capture cross section at 0.025 eV (barn)	B-10: 3837 B-11: 0.005	Ni58: 4.503 Ni60: 2.9

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Presentations:

1. Srisukvatananan, P., Arbeau, N., Lister, D.H., and Hussein, E.M.A. (2004, October 3-6) The Interaction of Dissolved Boron with Corrosion Products Deposited on Heated Surfaces in High Temperature Boiling Water. Paper presented at 54th Canadian Chemical Engineering Conference, Calgary, Canada.