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APPENDICES

Appendix A The Standard Color of Some Iron Oxides (Cornell, 2003)

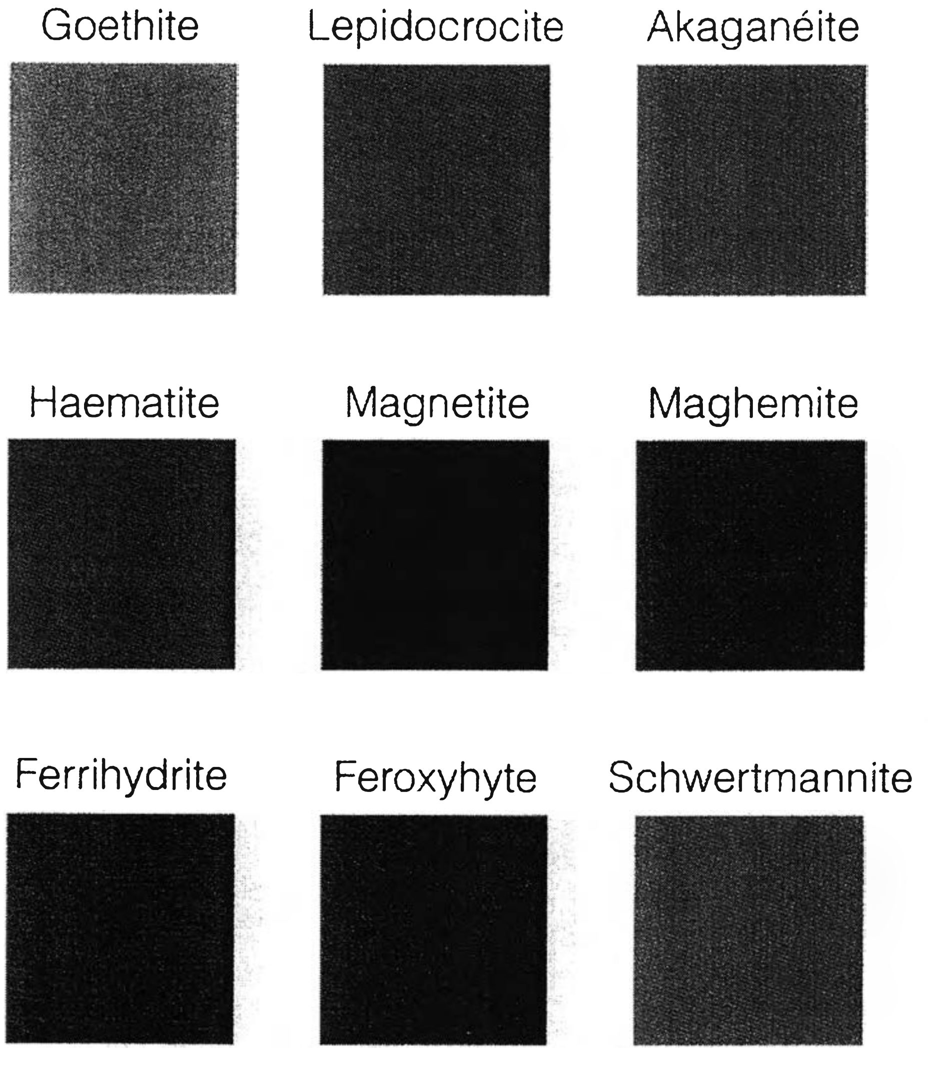


Figure A The standard color of some iron oxides.

Appendix B Energy-Dispersive X-ray Analysis Results

The elemental analysis data from Energy-Dispersive X-ray Analysis for both platinum films formed on the inside and outside carbon steel surfaces are shown in Table B.

Table B.1 Energy-Dispersive X-ray analysis results for platinum-coated inside surface of carbon steel

Selected Area	Fraction (Weight %)								
	Pt	**Fe**	**O**	**C**	**Na**	**Cl**	**Si**	**Cr**	**Total**
Figure 4.9a									
Spctrum 1	7.28	65.65	22.22	3.09	1.51	0.25	-	-	100
Figure 4.9b									
Spectrum 1	10.22	65.90	21.91	1.44	0.42	0.11			100
Spectrum 2	4.65	94.71	-	-	0.48	0.16			100
Spectrum 3	17.46	78.59	-	2.83	0.85	0.27			100
Figure 4.9c									
Spectrum 1	5.81	91.59	-	1.95	0.51	0.14	-	-	100
Spectrum 2	4.53	70.55	23.17	1.42	0.28	0.05			100
Spectrum 3	3.68	93.71	-	2.06	0.42	0.13			100
Figure 4.9d									
Spectrum 1	3.41	93.1	-	3.49	-	-	-	-	100
Spectrum 2	-	94.65	-	5.35	-	-	-	-	100
Mean	7.13	83.16	22.43	2.70	0.64	0.16	-	-	100

Table B.2 Energy-Dispersive X-ray analysis results for platinum-coated outside surface of carbon steel

Selected Area	Fraction (Weight %)								
	Pt	Fe	O	C	Na	Cl	Si	Cr	Total
Figure 4.10a									
Spectrum 1	27.38	72.14	-	-	0.40	0.08	-	-	100
Spectrum 2	24.32	70.33	-	4.7	0.42	0.14	-	0.09	100
Spectrum 3	17.05	78.17	-	3.54	0.33	0.07	0.26	0.58	100
Spectrum 4	14.68	84.54	-	0.73	-	-	-	0.05	100
Figure 4.10b									
Spectrum 1	63.46	31.25	-	3.21	1.09	0.31	-	0.68	100
Spectrum 2	27.79	68.62	-	2.57	0.6	0.19	-	0.23	100
Spectrum 3	23.94	73.09	-	2,30	0.5	0.17	-	-	100
Spectrum 4	26.59	68.93	-	2.54	1.14	0.3	0.4	0.1	100
Mean	28.15	68.38	-	2.80	0.64	0.18	0.33	0.29	100

Appendix C Raman Shift of Haematite in Different Studies

Table C Raman shift of haematite in different studies

Reference	**Raman Shift (cm^{-1})**								
T. Ohtsuka *et al.*, 1986	225 (s)	245 (m)	295 (s)		415 (s)	500 (w)	615 (m)		1320 (w)
R.J. Thibeau *et al.*, 1978	227	245	293	298	414	501	612		
R.K. Singh *et al.*, 1998			290		410	505	621	670	1320-1330
			293		415, 412	500	613		
			293		414	501	612		
D. Thierry *et al*, 1988	226	245	293	298	413	500	612		
	225	247		299	412	500	613		

* s refers to strong peaks

m refers to medium peaks

w refers to weak peaks

underline refers to strongest peaks

Appendix D Hydrogen Diffusion Coefficient in Carbon Steel Tube

Hydrogen diffusion for cylindrical coordinate equation:

$$m = \frac{dn}{dt} = -\frac{2\pi l D_{H_2} \Delta C}{\ln(r_2 / r_1)}$$

The ideal gas is applied to estimate the changing moles in hydrogen diffusion and concentration of hydrogen in the tube.

$$\frac{dn}{dt} = \frac{V}{RT}\frac{dP}{dt}$$

And
$$C = \frac{n}{V} = \frac{P}{RT}$$

So, the equation for hydrogen diffusion through the tube is $D_{H_2} = \dfrac{V \ln\left(\frac{r_2}{r_1}\right) \ln\left(\frac{P_1}{P_2}\right)}{2\pi l t}$.

The hydrogen diffusivity in tube can be calculated from the equation above. It is assumed that the thickness of platinum film formed on the carbon steel tube is so small for calculation of hydrogen diffusivity in platinum-filmed tube.

The calculated hydrogen diffusivity in carbon steel tube coated with platinum on both the inside and outside surfaces is shown below.

Total volume of hydrogen gas in the system

Volume of hydrogen gas in filmed carbon steel tube:

$$V = \frac{\pi d^2 l}{4} = \frac{(3.1416)(0.6223cm)^2(12cm)}{4} = 3.65cm^3$$

Volume of hydrogen gas in copper tube:

$$V = \frac{\pi d^2 l}{4} = \frac{(3.1416)(0.6629cm)^2(19cm)}{4} = 6.56cm^3$$

Volume of hydrogen gas in stainless steel tube:

$$V = \frac{\pi d^2 l}{4} = \frac{(3.1416)(0.7036cm)^2(17.35cm)}{4} = 6.75cm^3$$

Volume of hydrogen gas in brass fitting:

$$V = \frac{\pi d^2 l}{4} = \frac{(3.1416)(0.6223cm)^2(3cm)}{4} = 0.91cm^3$$

Therefore, the total volume of hydrogen gas in the system is 17.87 cm^3.

Pressure of hydrogen gas in tube

$$P_1 = (101.325kPa)\left(\frac{125 + 14.7psia}{14.7psia}\right) = 962.93kPa$$

$$P_2 = (101.325kPa)\left(\frac{12 + 14.7psia}{14.7psia}\right) = 184.04kPa$$

Hydrogen diffusivity in carbon steel tube coated with platinum on the inside and outside surfaces

$$D_{H_2} = \frac{V \ln\left(\frac{r_2}{r_1}\right)\ln\left(\frac{P_1}{P_2}\right)}{2\pi l t}$$

$$D_{H_2} = \frac{(17.87 \times 10^{-6} m^3)\ln\left(\frac{4.7625 \times 10^{-3} m}{3.1115 \times 10^{-3} m}\right)\ln\left(\frac{962.93kPa}{184.04kPa}\right)}{2(3.1416)(0.15m)(4.25 \times 3600s)} = 8.73 \times 10^{-10}\, m^2/s$$

The hydrogen diffusivity calculation was done in the same manner as shown above for other cases; uncoated carbon steel tube, platinum film formed on the either inside or outside surface and platinum film formed on both the inside and outside surfaces.

Appendix E Surface Resistance on Carbon Steel Tube and Estimated Surface Resistance on The Feeder Pipes at Point Lepreau Generating Station (PLGS)

Overall surface resistance equation: $\frac{dn}{dt} = -\frac{A_i \Delta C}{R_t}$

The ideal gas is applied to estimate the changing moles in hydrogen diffusion and concentration of hydrogen in the tube.

$$\frac{dn}{dt} = \frac{V}{RT}\frac{dP}{dt}$$

And
$$C = \frac{n}{V} = \frac{P}{RT}$$

Therefore, the equation for overall surface resistance becomes $R_t = \frac{A_i t}{V \ln\left(\frac{P_1}{P_2}\right)}$

that is equal to the summation of the outside surface resistance, inside surface resistance and metal resistance; $R_t = R_o + R_m + R_i$.

Where
$$R_m = \frac{A_i \ln\left(\frac{r_2}{r_1}\right)}{2\pi D_{H_2} l}$$

The calculation to determine resistance to hydrogen transport through tube is shown below.

By coating platinum on the inside surface of carbon steel tube only, the inside surface resistance is assumed to be eliminated. Since the average hydrogen diffusivity at 306°C of tube surface temperature is known (8.44×10^{-10} m^2/s). The outside surface resistance can be determined from the experiment.

Overall surface resistance

$$R_t = \frac{A_i t}{V \ln\left(\frac{P_1}{P_2}\right)}$$

$$R_t = \frac{(2.9325\times10^{-3}m^2)(5.33\times3600s)}{(17.87\times10^{-6}m^3)\ln\left(\frac{949.15kPa}{187.49kPa}\right)} = 1.94\times10^6\ s/m$$

And $$R_t = R_o + R_m$$

Outside surface resistance

$$R_o = R_t - \frac{A_i \ln\left(\frac{r_o}{r_i}\right)}{2\pi D_{H_2} l}$$

$$R_o = 1.94\times10^6 - \frac{(2.9325\times10^{-3}m^2)\ln\left(\frac{4.7625\times10^{-3}m}{3.1115\times10^{-3}m}\right)}{2(3.1416)(8.44\times10^{-10}m^2/s)(0.15m)} = 3.72\times10^5\ s/m$$

Therefore, the outside surface resistance in this experiment is $3.72\times10^5\ s/m$. The calculation of the outside surface resistance in another experiment was carried out the same manner as shown above.

On the other hand, by coating platinum on the outside surface of carbon steel tube only, the outside surface resistance is assumed to be eliminated. Since the average hydrogen diffusivity at 306°C of tube surface temperature is known (8.44×10^{-10} m^2/s). The inside surface resistance can be determined from the experiment.

Overall surface resistance

$$R_t = \frac{A_i t}{V \ln\left(\frac{P_1}{P_2}\right)}$$

$$R_t = \frac{(2.9325\times10^{-3}m^2)(5\times3600s)}{(17.87\times10^{-6}m^3)\ln\left(\frac{956.04kPa}{194.38kPa}\right)} = 1.85\times10^6\ s/m$$

And $$R_t = R_o + R_m$$

Inside surface resistance

$$R_i = R_t - \frac{A_i \ln\left(\frac{r_o}{r_i}\right)}{2\pi D_{H_2} l}$$

$$R_i = 1.85\times10^{6} - \frac{\left(2.9325\times10^{-3} m^2\right)\ln\left(\frac{4.7625\times10^{-3} m}{3.1115\times10^{-3} m}\right)}{2(3.1416)(8.44\times10^{-10} m^2/s)(0.15m)} = 2.85\times10^{5}\ s/m$$

So, the inside surface resistance in this experiment is $2.85\times10^{5}\ s/m$. The calculation of the inside surface resistance in another experiment was carried out the same manner as shown above.

In addition, since the hydrogen diffusivity is known ($8.73\times10^{-10}\ m^2/s$). The resistance of the carbon steel tube itself can be determined from the carbon steel tube coated with platinum on both the inside and outside surfaces.

$$R_m = \frac{A_i \ln\left(\frac{r_2}{r_1}\right)}{2\pi D_{H_2} l}$$

$$R_m = \frac{\left(2.9325\times10^{-3} m^2\right)\ln\left(\frac{4.7625\times10^{-3} m}{3.1115\times10^{-3} m}\right)}{2(3.1416)(8.73\times10^{-10} m^2/s)(0.15m)} = 1.52\times10^{6}\ s/m$$

The determination of the resistance of the carbon steel tube itself from another experiment was calculated in the same way.

Furthermore the resistance of the feerder pipe in the plant was estimated using the measured average hydrogen diffusivity in this study at the tube surface temperature of 306°C. The calculation below shows the resistance of the feeder pipe of 6 mm of wall thickness.

$$R_t = \frac{l}{D_{H_2}} = \frac{6\times10^{-3} m}{8.44\times10^{-10} m^2/s} = 7.10\times10^{6} s/m$$

The estimation of the resistance of the feeder pipe of 5 mm of wall thickness was calculated in the same manner as shown above.

Appendix F Estimated Hydrogen Diffusivity in Nickel-Alloy (Hastelloy-C) and Carbon Steel Tube Outside The Furnace Replaced With Copper Tube

In order to estimate the hydrogen diffusivity in nickel-alloy (Hastelloy-C) and carbon steel tube outside the furnace replaced with copper tube, it is assumed that the average outside surface resistance and inside surface resistance on nickel-alloy tube and carbon steel tube outside the furnace replaced with copper tube are equal to that on the platinum-filmed carbon steel tube surface.

The estimetd hydrogen diffusivity in nickel-alloy (Hastelloy-C) is shown below.

Overall surface resistance on nickel-alloy (Hastelloy-C)

$$R_t = \frac{A_i t}{V \ln\left(\frac{P_1}{P_2}\right)}$$

$$R_t = \frac{(3.7341\times10^{-3} m^2)(263.67\times3600 s)}{(19.01\times10^{-6} m^3)\ln\left(\frac{907.79 kPa}{597.61 kPa}\right)} = 4.46\times10^{8}\ s/m$$

And $$R_t = R_o + R_m + R_i$$

Nickel-alloy resistance and hydrogen diffusivity in nickel-alloy

$$R_m = R_t - R_o - R_i$$

$$R_m = 4.46\times10^{8} - 3.85\times10^{5} - 3.17\times10^{5} = 4.45\times10^{8}\ s/m$$

Where $$R_m = \frac{A_i \ln\left(\frac{r_2}{r_1}\right)}{2\pi D_{H_2} l}$$

So, $$D_{H_2} = \frac{A_i \ln\left(\frac{r_2}{r_1}\right)}{2\pi l R_m}$$

$$D_{H_2} = \frac{\left(3.7341\times10^{-3}m^2\right)\ln\left(\dfrac{4.7625\times10^{-3}m}{3.1115\times10^{-3}m}\right)}{2(3.1416)(0.19m)(4.46\times10^{8}\,m^2/s)} = 2.97\times10^{-12}\,s/m$$

The estimated hydrogen diffusivity in nickel-alloy (Hastelloy-C) is $2.97\times10^{-12}\,m^2/s$.

The hydrogen diffusivity in carbon steel tube outside the furnace replaced with copper tube was calculated the same way as shown above.

Appendix G Estimation of Time Before Hydrogen Pressure Inside The Carbon Steel Drop at Room Temperature

The concentration-time chart for a large flat slab is used to estimate the time before hydrogen pressure inside the carbon steel tube drop at room temperature in order to confirm that there is no hydrogen leak at room temperature for 2 days of leak test. This calculation relies on the following assumptions:

1. The convective mass transfer coefficient of hydrogen is very large relative to hydrogen diffusion coefficient. Therefore, the convective mass transfer coefficient is negligible, m = 0.
2. The hydrogen concentration is measured at the centre of tube, n = 0.
3. The hydrogen concentration at the tube surface is zero.
4. The hydrogen diffusion through the tube surface is similar to that in a large flat slab.
5. The initial hydrogen pressure inside the tube is 100 psig and the hydrogen pressure inside the tube at the end is 99 psig if there is a leak, Y = 0.99.

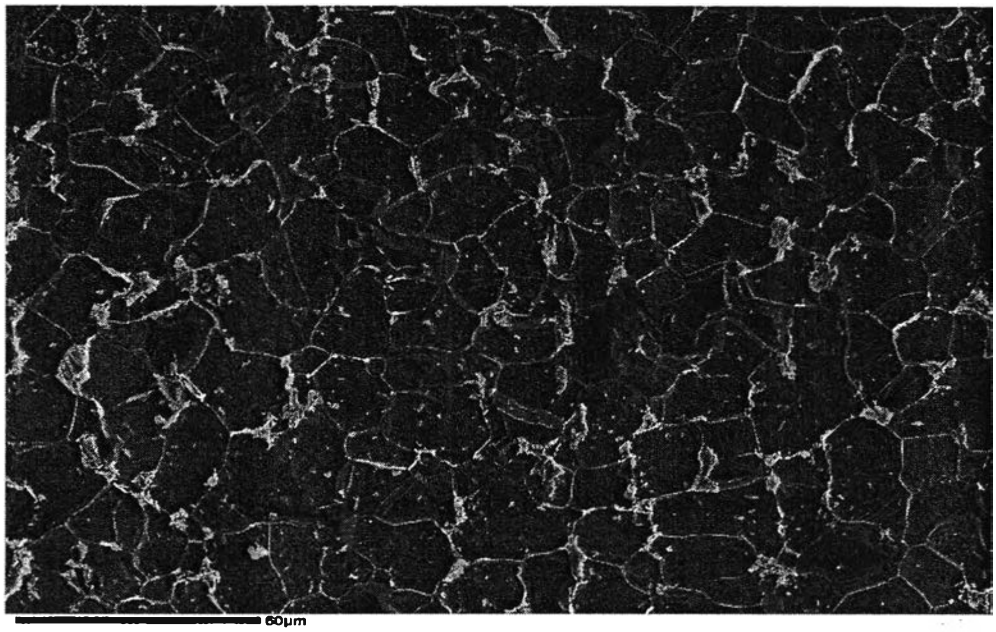
From the concentration-time chart for a large flat slab, the relative time (X) is 0.2.

Where
$$X = \frac{D_{H_2} t}{x_1^2}$$

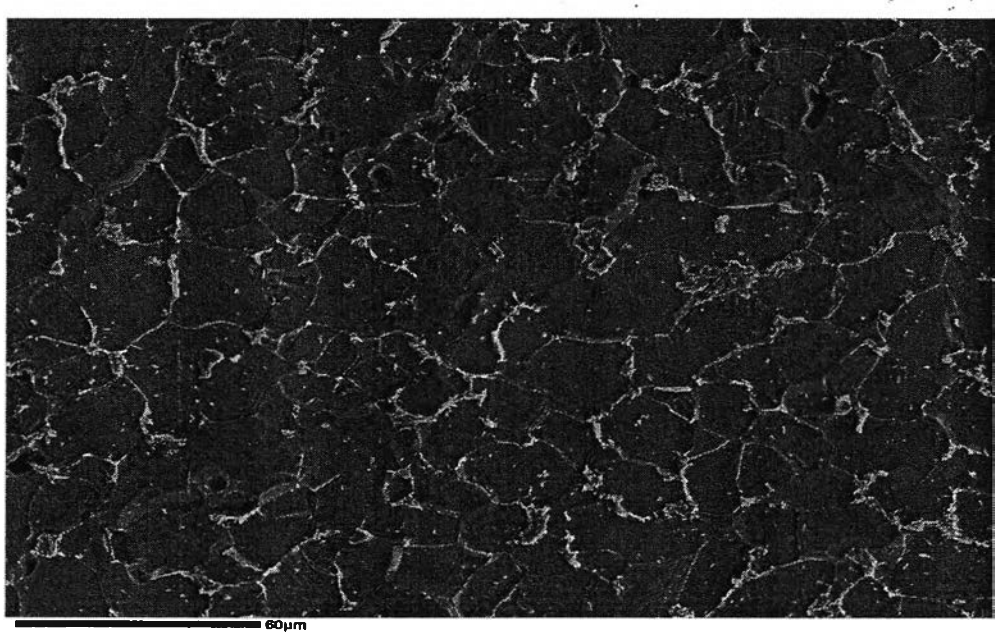
$$t = \frac{X x_1^2}{D_{H_2}} = \frac{(0.2)(1.651\times10^{-3} m^2)}{(1.39\times10^{-10} m^2/s)} = 3{,}922.01 s$$

The estimated time required for hydrogen pressure drop 1 psig is 3,922.01 s or 1.09 h. But the leak test at room temperature for 2 days in this study shows that the hydrogen pressure inside the tube is essentially constant indicating there is no leak. This might be partially explained by the molecular hydrogen cannot dissociate to atomic hydrogen at room temperature.

Appendix H Structure and Hardness of Carbon Steel Tube (ASTM A179)



(a) Grain structure along the length of a carbon steel tube, hardness: 55.5



(b) Grain structure of a carbon steel tube in cross section direction, hardness: <30

Figure H Grain structure of carbon steel tube (ASTM A179).

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