CHARACTERIZATION OF BRUCE POWER UNIT 6 PREHEATER TUBE OXIDE

Aamir Husain, Alan Mcbride,
Kinectrics Inc.

ABSTRACT

The primary oxide on three sections from Unit 6, Steam Generator 4 Preheater, cold leg side straight length tubing was chemically and radio-chemically characterized. The data were required partially in support of the primary side clean of Unit 5 steam generators in Fall ’05 and partially to enhance our understanding of the characteristics of oxide deposits.

The oxide consisted principally (97 wt %) of magnetite; other elements present in the magnetite structure included chromium, nickel, cobalt, copper and titanium.
Across the thickness of the oxide layer, the relative levels of chromium and nickel were similar to that present in the base metal. The magnetite loading ranged between 190 and 340 g/m^2. Over a tube length of approximately 2.2 m, the thickness of oxide increased from 60 μm near the C07 support plate to 112 μm near the cold leg tubesheet.

Co-60 was the dominant gamma emitting radionuclide present in the preheater oxide. The specific activity of Co-60 generally decreased with oxide thickness as the base metal interface was approached. Non-gamma emitting radionuclides, namely, Fe-55, Ni-63 and transuranics were also quantified. Their scaling factors were generally consistent with those previously obtained from characteristics of steam generator oxides.

1.0 INTRODUCTION AND BACKGROUND

Steam generators at Bruce, unlike those at Pickering and Darlington, are equipped with external feed water preheaters. Outgoing heavy water from each steam generator flows through an Inconel 600 tubed preheater thus raising the temperature of the feed water before it enters the steam generator.

Straight sections of a tube (R 30 C21) were pulled on September ‘04 (Effective Full Power Years =15.36) from the cold leg side of the preheater associated with Unit 6 Steam Generator 4. Three of the seven pieces removed, namely, Section #2, Section #4 and Section #7 were characterized as follows

- A 15 cm section of each piece was characterized by dissolving the oxide to determine oxide loading (g/cm^2), radioactivity loading (nCi/mg) and elemental loading (g element/g deposit). Profiles of the elemental and the radioactivity loadings across the oxide layer were developed.

- A 5 cm section of each piece was sectioned for metallographic examination to determine the thickness of the ‘as is’ oxide.

The data were required partially in support of the primary side clean of Unit 5 steam generators in Fall ’05 and partially to enhance our understanding of the characteristics of oxide deposits.

Figure 1 illustrates the location of the three sections characterized relative to the tube sheet. The C01 support plate is 381 mm from the tube sheet. The distance between successive support plates until C06 is 322 mm; the spacing between C07 and C08 is 378 mm and that between C08 and C09 (the last support before the U bend region) is 183 mm.

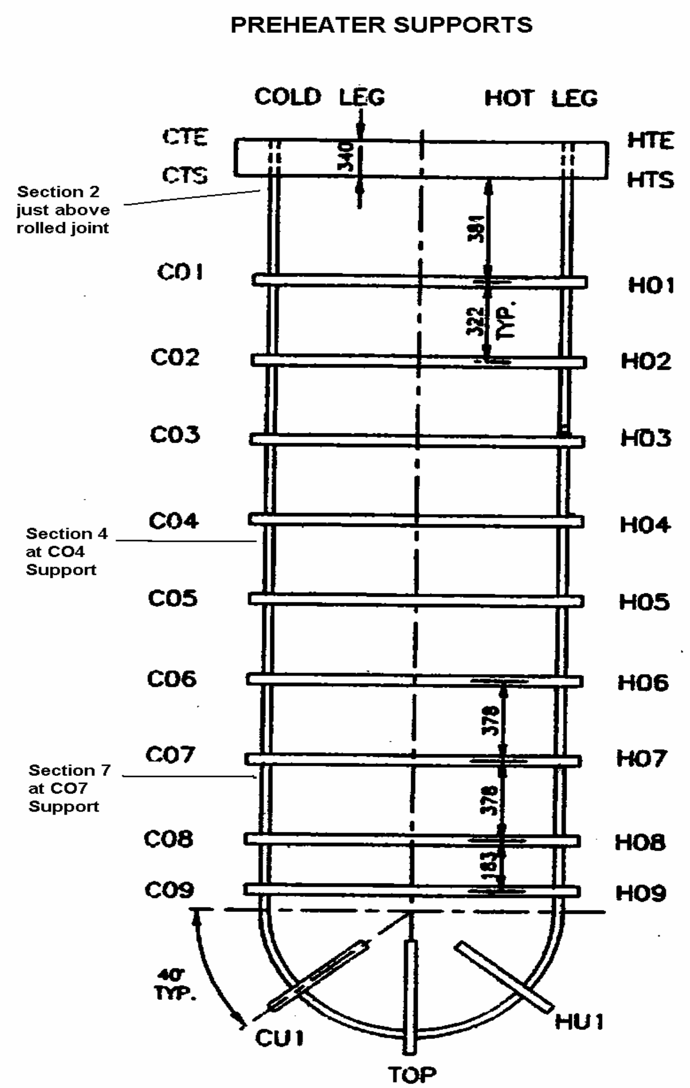

Figure 1: Schematic of Preheater Showing the Location of Sampled Tube Sections

2.0 EXPERIMENTAL – OXIDE DISSOLUTION

The internal lengths of each 15 cm tube section were exposed to concentrated hydrochloric acid to dissolve the primary side oxide. The tube was repeatedly filled with acid and drained until dose rate reduction and the absence of color in the drained liquid signaled the end of the oxide dissolution. The successive acid exposures were of controlled time duration (ranging from 15 s to 5 min) and each batch of liquid drained from the tube was segregated. Up to about 21 separate batches were collected. Each batch was analyzed for its elemental and radioactivity loading.

Prior to the initial acid exposure, the tube was flushed with water to remove any loose oxide and cutting debris present. Following the last acid exposure, a water rinse was performed to account for the oxide constituents associated with the residual acid on the tube surfaces.

The tubes were weighed before and after the final exposure to correlate the amount of dissolved oxide (as determined from the ICP-MS data) with the weight loss experienced. The tubes were finally cut open along their lengths to assess the completeness of oxide dissolution.

3.0 CHARACTERIZATION RESULTS – METALLOGRAPHIC EXAMINATION

Measured oxide thicknesses based on metallographic examination of Tube Section #s 2, 4 and 7 are summarized in Table 1 below.

Table 1: Measured Thickness of Internal Oxide

Tube Section #	Measured Oxide Thickness (μm)
2	112
4	81
7	60

The oxide thickness appears to increase in the direction of flow, Tube Section #2 and #7 being closest and furthest away from the tube sheet, respectively. This is consistent with the water being saturated (with iron) to the greatest degree at Section #2 where the temperature is the lowest and least at Section #7 where the temperature is highest. Thus, progressively increasing deposits occur along the flow path.

4.0 CHARACTERIZATION RESULTS – CHEMICAL COMPOSITION

As stated earlier, the successive acid drainings from each tube were analyzed using ICP to determine the elemental composition of the oxide. The elements analyzed included Fe, Cr, Ni, and Co. These are typically expected in the PHT system with Fe, Cr and Ni also being the principal constituents of the preheater tube base metal. Ti was also analyzed because of its significance in flow assisted corrosion of carbon steel feeders.

As expected, iron was the dominant element present in the oxide. The levels of iron were converted into the equivalent quantity of magnetite assuming the contribution from base metal corrosion to be negligible. The results are shown in Table 2. Note the following:

- Comparison of the weight of magnetite determined from the elemental compositions of the solutions with the weight loss experienced during the acid exposures indicated a reasonable agreement particularly for Section #s 4 and 7. The approximately 10% discrepancy in the case of Section #2 could not be rationalized.

- The corresponding magnitude of the oxide loadings is consistent with the range the oxide loadings previously measured on BNGS Unit 3 SG 2 (5-200 g/m^2) and BNGS Unit 5 SG 5 (38-209 g/m^2) tubing [Husain and Krasznai 2005].

- Table 2 also shows the overall porosity value for each tube section. The value was obtained by comparing the oxide thickness calculated from the amount of dissolved oxide (Column 3 in Table 2) with the value obtained from metallographic examination (see Table 1). As shown, the oxide porosity varied between 50 and 60 % for the three tube sections with an average being approximately 56%.

Table 2: Oxide Loading and Estimated Porosity of Preheater Oxide

Tube Section #	Measured Weight Loss (g)	Weight Loss Based on Analysis of Solutions (g)	Oxide Loading (g/m^2)	Estimated Porosity (%)
2	1.9489	1.73	340	57
4	1.0820	1.07	220	50
7	0.9492	0.96	190	60

Elemental profiles obtained from the ICP results are plotted in Figure 2. These indicate the following:

- The concentrations of nickel and chromium were essentially constant across the oxide layer but increased sharply as the base metal was approached. Thus corrosion was not a significant contributor to the measured concentrations of nickel and chromium during the successive acid exposures. The ratio of Cr/Ni across the oxide layer was, however, essentially constant and comparable with the value of 0.21 in the base metal. The Inconel tubing is thus the likely source of Cr and Ni in the oxide.

- In contrast, the Fe/Ni ratio was variable across the oxide layer (as high as 217 in the case of Section 2). The measured Fe/Ni ratios at the end of the exposures (23, 2.1 and 4.4 for Sections #2, #4 and #7, respectively) were still significantly greater than the value of ~ 0.11 in the base metal. Thus, the dissolved metals in solution originated predominantly from the oxide layer and not from the base metal. The relatively high Fe/Ni ratio observed at the end of the acid exposures is consistent with the presence of residual oxide noted on the acid exposed tube sections (the sections were split after the acid exposures).

- The concentration of elemental cobalt was essentially constant (order of 10^{-5} g/g magnetite) across the oxide layer but increased at the oxide-metal interface. This is indicative of the diffusion of cobalt from the base metal into the oxide although deposition may also occur from solution.

- As in the case of cobalt, the level of titanium across the oxide layer was also constant but increased significantly at the oxide-metal interface suggesting that the Inconel 600 base metal is the likely source for titanium. The titanium/magnetite mass ratio for the bulk preheater oxide was approximately 1.1E-04. This value is somewhat lower than that previously obtained for Incoloy 800 tubed steam generator oxide at Darlington.

The dissolution rate of the oxide was calculated from the amount of oxide dissolved in each exposure. The data, illustrated in Figure 3, indicates that initially the rate decreased sharply and then leveled off. Two possible contributing factors for these observations are:

- Diffusion of Ni and Cr from the base metal possibly leads to the increased formation of ferrites as the base metal is approached; the ferrites have a lower solubility than magnetite.

- Possibly, as a result of the incorporation of depositing species from solution (principally iron), the oxide porosity decreases as the base metal is approached.

5.0 CHARACTERIZATION RESULTS - RADIOCHEMICAL

Results of the overall radiochemical characterization are summarized in Table 3. Co-60 dominated the gamma activity of the oxide. Compared to it, the activity of Fe-55, a low energy X-ray emitter, was significantly higher. Among the various transuranics (alpha emitters Pu-238, Pu-239+240, Am-241 and Cm-244 and beta emitter Pu-241), the activity of Pu-241 was relatively high. The beta emitters C-14 and Sr-90 were not characterized; their levels are, however, expected to be much lower than that of Fe-55.

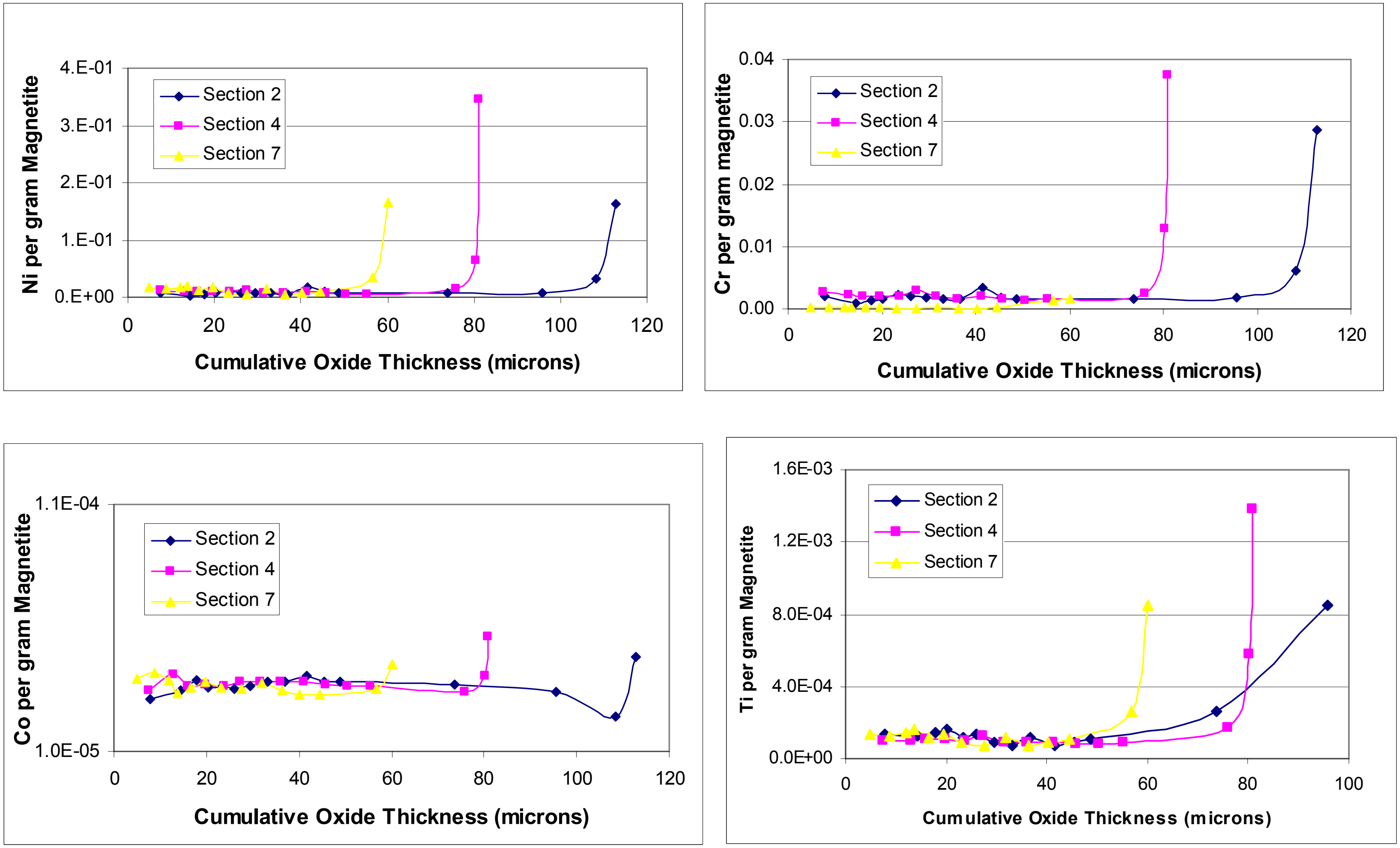

Figure 2: Elemental Distributions Across the Oxide Layers
(oxide thickness is considered zero at the oxide-water Interface)

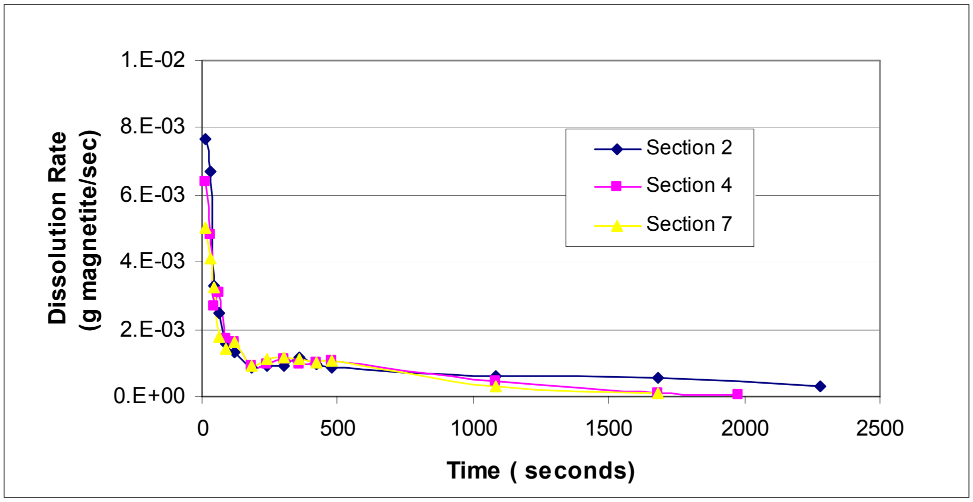

Figure 3: **Rate of Oxide Dissolution as a Function of Time**

Table 3: Radionuclide Activity Data for Preheater Tube Sections

Radionuclide	Radionuclide Activity* (Bq/g Magnetite)		
	Tube Section #2	**Tube Section #4**	**Tube Section #7**
Mn-54	4.1E+03	5.2E+03	5.2E+03
Co-60	2.6E+05	3.0E+05	3.1E+05
Nb-94	1.7E+03	1.4E+03	1.2E+03
Zr-95	7.8E+04	1.0E+05	6.7E+04
Sb-124	-	7.0E+04	5.2E+04
Sb-125	1.0E+04	5.6E+03	3.7E+03
Fe-55	1.3E+06	1.3E+06	1.3E+06
Ni-63	1.6E+03	2.3E+03	3.0E+03
Pu-241	2.1E+02	2.7E+02	3.8E+02
Pu-238	2.4E+00	2.3E+00	2.9E+00
Pu-239+Pu-240	1.3E+01	1.8E+01	2.4E+01
Am-241	2.1E+01	2.6E+01	3.3E+01
Cm-244	4.5E+01	5.8E+01	6.1E+01

*Activity was decay corrected to September 2004, the tube pull date

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The specific activity of Co-60 in the preheater oxide appears to decrease slightly in the direction of flow although from a practical standpoint it may be considered to be more or less constant. This behavior is consistent with trends observed in CANDU steam generators [Husain and Krasznai 2005], both with and without integral preheaters, where typically the specific activity decreases sharply over a 5m tube length (measured from the primary side, hot leg, tube sheet face) in the hot leg and then gradually levels off. The external preheaters at Bruce may thus be considered as extensions of their associated steam generators.

The measured Co-60 specific activity values are, however, significantly lower than the values measured in the cold legs of Bruce Unit 5 SG 5 (1.3E+06 Bq/g at EFPY 8.1 y) and Bruce Unit 3 SG 2 (8.5E+05 Bq/g at EFPY 11.8 y) tubes in 1994. This may arise if the deposition rate of Co-60 associated with newly formed oxide is lower than its rate of decay in the previously deposited oxide, thus resulting in an overall decrease in Co-60 specific activity with elapsed time or EFPY.

Scaling factors are widely used to estimate the activities of Difficult-to-Measure alpha/beta emitting radionuclides from the activities of Easy-to-Measure gamma emitting radionuclide such as Co-60 [Husain 2005]. Scaling factors calculated from the data in Table 3 are shown in Table 4 where LM and LD refer to Log Mean and Log Dispersion (LD), respectively. As shown by the low LD values, the data for the three tube sections are reasonably consistent (agreement to within a factor of 1.7). For comparison, scaling factors based on Oxiprobe data for Bruce steam generators are also included in Table 4. In general, the agreement between the two data sets is reasonably good confirming that the characteristics of the preheater tube oxide are generally consistent with those of the steam generator oxides.

Table 4: Scaling Factors for Preheater Tube Oxide

	Preheater Tube Oxide		Steam Generators	
Scaling Factor	**LM**	**LD**	**LM**	**LD**
(Pu-239+Pu-240)/Co-60	6.2E-05	1.3	1.2E-04	2.8
(Pu-239+Pu-240)/Sb-125	3.1E-03	1.7	1.0E-02	1.9
Pu-238/(Pu-239+Pu-240)	1.4E-01	1.3	3.9E-01	1.6
Pu-241/(Pu-239+Pu-240)	1.6E+01	1.1	-	-
Am-241/(Pu-239+Pu-240)	1.5E+00	1.1	1.1E+00	2.0
Cm-244/(Pu-239+Pu240)	3.0E+00	1.2	1.2E+00	3.2
Fe-55/Co-60	4.5E+00	1.1	4.3E+00	1.4
Ni-63/Co-60	7.8E-03	1.3	-	-

The variation of Co-60 activity across the oxide layer is of interest because the achievable decontamination factor (DF) during mechanical cleaning of steam generators is determined by the distribution of Co-60 activity in the oxide layer. Figure 4 shows the variation of Co-60 activity in the oxide as a function of its thickness (the oxide-water interface is considered as the reference plane, i.e., the oxide thickness is considered to be zero at this plane). The variation for Tube Sections #4 and 7 is distinctly different from that for Tube Section #2. These specific activity profiles are possibly indicative of perturbations in the iron and Co-60 content of the primary water in recent years. Without such perturbations, newly depositing oxide would have a constant specific activity and if the rate of deposition is low, the cumulative activity may decrease with EFPY or equivalently oxide thickness in accordance with radioactive decay. Such a behavior has previously been observed in Darlington steam generator tube oxide.

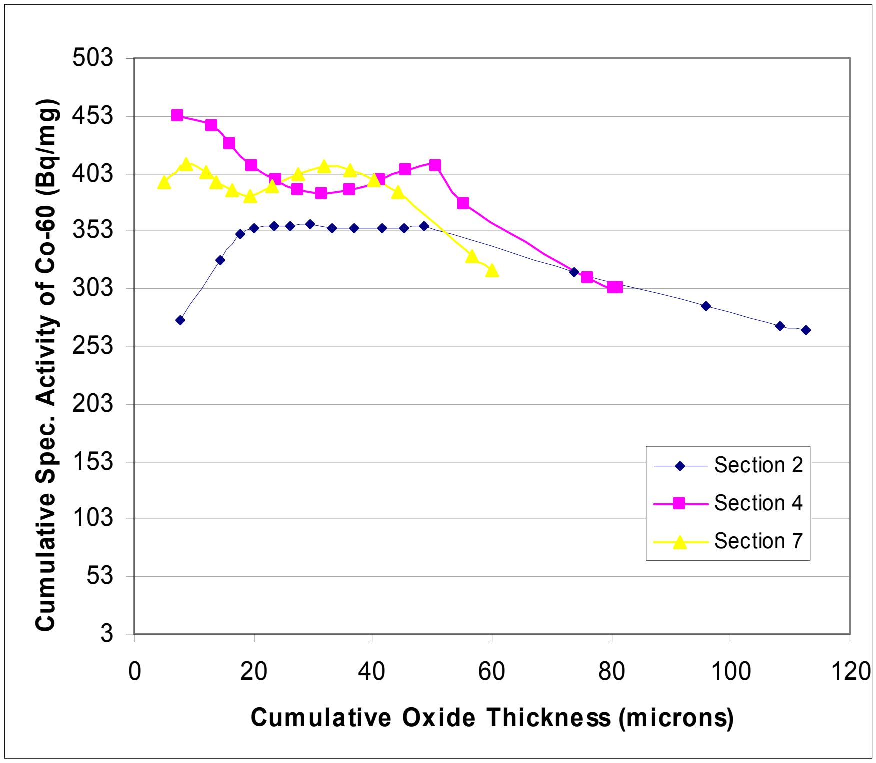

Figure 4: Variation of Co-60 Specific Activity with Oxide Thickness
(oxide thickness is considered zero at the oxide-water Interface)

6.0 CONCLUSIONS

- The oxide consists principally (97 wt %) of magnetite; besides iron, other elements present in the magnetite structure include chromium, nickel, cobalt, copper and titanium.

- The overall porosity of the oxide ranged between 50% and 60%.

- The thickness of oxide increased systematically with tube length possibly because of the increased saturation of the solution with iron. Over a tube length of approximately 2.2 m, the thickness increased from 60 µm to 112 µm. The corresponding magnetite loading ranged between 190 and 340 g/m^2.

- The rate of oxide dissolution decreased sharply with oxide thickness and then leveled off as the metal-oxide interface was approached. This is possibly because of the increasing levels of ferrites and the reduced porosity of the oxide as the metal interface is approached.

- Across the thickness of the oxide layer, the relative levels of Cr and Ni were similar to that present in the base metal. These elements are thus considered to arise by diffusion from the base metal.

- Titanium was also observed in the oxide and likely arises from a trace impurity in the base metal. A similar comment applies to inactive Co although this element may also be deposited from solution.

- Co-60 was the dominant gamma emitting radionuclide observed in the oxide. The oxide also contained varying levels of difficult-to-measure, non-gamma emitters such as Fe-55, Ni-63 and transuranics.

- The measured specific activity of Co-60 varied between 2.4E+05 and 2.9E+05 Bq per magnetite. This value is significantly lower than the value of 1.3E+06 Bq/g previously measured for BNGS Unit 5 SG 5 tubing.

- Despite some inconsistencies, in particular over the outer oxide layer, the specific activity of Co-60 generally decreased over most of the oxide layer.

- Measured scaling factors for the difficult-to-measure radionuclides present in the preheater oxide are in reasonable agreement with those previously determined for Bruce B steam generators. These data can, therefore, be applied to estimate the inventory of alpha/beta emitting radionuclides in the steam generators based on applicable values for the Co-60 activity.

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