CHARACTERISTICS OF WEAR PRODUCTS FROM FUELING MACHINE RAM BALLS AT DARLINGTON

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ABSTRACT

Introduction of dissolved and particulate Stellite ram balls wear products into the primary heat transport system during fueling machine on-power channel operations may result in a significant additional contribution to the reactor Co-60 fields. The heavy water auxiliary system (HWAS) associated with each Darlington fueling machine (FM) trolley is currently equipped only with a 1 μm filter; despite a roughed-in provision, no ion exchange purification is employed. Minimizing the introduction of ram balls wear products into the Primary Heat Transport (PHT) system by more effective filtration and by using ion exchange columns in the HWAS would reduce their contribution to the Co-60 source term.

This paper presents an assessment of the adequacy of the present filter and the benefit of installing ion exchange capability in the HWAS. These assessments were performed by analyzing samples of FM water drawn from the HWAS. Both the loading and the particle size distribution of Stellite wear products in the samples were determined. Following successive filtration through a range of filter sizes down to 0.1 μm, the filtered water samples were exposed to mixed bed ion exchange resins to determine the dissolved ionic loading present.

In addition, smears taken from filter housings during filter change-out and a cut-out sample from a spent filter were analysed to determine the elemental compositions and gamma activity make-up of the particulate present. These data were combined with dose rate data for the corresponding spent filters to obtain estimates for the generation rate of ram balls wear product.

While the data developed were insufficient to assess the merits of replacing the current filter with a 0.1 μm filter, installation of a mixed bed ion exchange column in the HWAS would be beneficial and is, therefore, recommended.

1.0 INTRODUCTION AND BACKGROUND

Two fueling machines (FM), one at each reactor face, are used for on-line fueling of the CANDU reactor, i.e., to retrieve irradiated fuel from the reactor and replace them with new fuel bundles. Having serviced a reactor channel, the two trolley mounted FMs transport the irradiated fuel to the fuel bay and load up on new replacement fuel to prepare for a repeat duty at the reactor face.

The FM head is normally filled with non-pressurised heavy water which is supplied from the trolley mounted auxiliary system (HWAS). Its temperature is regulated in the main circulation loop of the HWAS using an air-cooled heat exchanger; an electric preheater is used to raise temperature for pressurization of the FM head. The main circulation loop at Darlington includes a filter housing equipped with a 1 μm filter. The Darlington HWAS is not presently equipped with ion exchange capability although a roughed-in provision exists in a side stream.

Preheating of the FM head and calibration of the head component forces, when required, take place at the start of the fueling cycle. Either one or both FM heads are then loaded with new fuel. Once the FM head is locked on to a channel end fitting, it is pressurized by the HWAS. Following a leak test, the channel closure and shield plugs are removed. With both FM heads in this condition, the required number of fuel bundles is then transferred. The FM may be operated in 3 modes:

- <u>Closed Loop Re-Circulation Mode:</u> Heavy water in the HWAS is re-circulated during all transition steps and during calibration runs.

- <u>Reactor Mode:</u> High pressure heavy water, drawn from the Primary Heat Transport (PHT) Feed & Bleed System is filtered and injected into the channel being refueled. Flow is injected into the channel while the closure plug is being withdrawn to prevent crud which has accumulated behind the outlet shield plug from being drawn into the FM.

- <u>Low Level Air Open Mode:</u> During fuel discharge into the bay, the FM head is locked onto the discharge port and the magazine rotated to line up two bundles with the snout, above the heavy water level. The FM ram, which is a part of the FM head, then transfers the bundles onto the shuttle of the discharge mechanism, which was earlier advanced into the FM head. The heavy water level in the FM head is adjusted using the fill and bleed system associated with the HWAS. To raise level, water is drawn from a storage tank in the HWAS and conversely discharged to the tank to lower the level.

During operation in the Reactor Mode, the ram remotely handles the fuel channel closure plugs, the shield plugs and the fuel. The main components of the ram are 4 ball screws which contain load balls made of Stellite Star-J material; the latter is principally constituted of Co (36% min), Cr (31-34 %) and W (16-19 %). A systematic reduction of the ball diameter occurs because of wear during service with the resulting wear products removed either by filtration in the HWAS or as a result of injection into the PHT system during fueling. Because the FM operates in re-circulation mode at least 40% of the time, filtered wear products can continue to undergo dissolution and subsequently be introduced into the PHT system as dissolved ionic cobalt.

Introduction of both dissolved and particulate ram balls wear product into the PHT system result in an increased contribution to the PHT Co-60 fields. The replacement of a previously spent and hence in-operative ion exchange column in the HWAS purification circuit at Gentilly-2 led to a dramatic reduction in PHT Co-60 fields at that plant [Guzonas 2007; Gauthier, P. and D. A. Guzonas 2005]. The present situation at Darlington, where the HWAS is not equipped with ion exchange capability, is not unlike that which previously existed at Gentilly-2. Therefore, it is likely that ram ball wear products are making a significant contribution to the Co-60 source term at Darlington. If so, reduction in the filter size and installation of ion exchange capability would reduce the ram ball Co-60 source term contribution.

This paper presents the findings from the characterization of ram balls wear products at Darlington. The study was undertaken to assess the adequacy of the present filter size and the need for installing ion exchange capability. The assessment was performed by measuring the particle size distribution of wear products in samples of HWAS water and by exposing the filtered water samples to ion exchange resins. In addition, estimates for the generation rate of ram balls wear product were developed based on measured spent filter dose rates and radiochemical/chemical analysis of filter housing smears.

2.0 SAMPLING OF FUELING MACHINE AND PRIMARY HEAT TRANSPORT SYSTEM WATER

Dissolved ram balls wear product is produced throughout the FM cycle time. However, particulate ram balls wear product will be produced primarily during operation of the FM ram. The latter is in operation when the FM is locked on to a channel, when spent fuel is being discharged at the fuel bay or new fuel is being loaded up and when the FM is in a calibration mode (this is infrequent). Most of the debris produced during the channel locked-on phase is likely flushed into the PHT system along with the injection flow. This is unavoidable. The debris produced during the remaining cycle time is continuously removed by the online filter in the HWAS. As a result, the best opportunity for collecting samples of HWAS water with elevated levels of particulate is immediately following the operation of the ram before the particulate is substantially removed by the online filter.

Because of high radiation fields, manual sampling of HWAS water is feasible only after irradiated fuel has been discharged at the fuel bay; sampling is not feasible during fueling operations. The HWAS water can be sampled at only two locations, namely, at Valve V10 upstream of the filter and at Valve V11 downstream of the filter. The V10 location potentially provides an unfiltered sample immediately after ram operation; delays in sampling would yield unfiltered samples at both the V10 and V11 locations.

Ten samples (FM1 to FM10) were collected from the HWAS as shown in Table 1. Additionally, two light water samples FM11 and FM12 were also collected from the Pressure Test Facility[1] (PTF) located in the FM Maintenance Area. FM11 was collected from V9 upstream of the filter while FM12 was collected from V51 located in a leg off the main process line, downstream of the filter and heat exchanger. Note that samples collected from V9, immediately after a calibration run, are expected to contain a higher concentration of particulate wear material than samples collected at V51.

In addition to the FM water samples, samples of PHT water were also collected for reference. They were collected at the outlet headers in both the North and South loops. Details are summarized in Table 2. Note that the PHT water will also contain contributions from other Co bearing PHT System components and also from corrosion products. If their contributions are relatively small compared with the contribution of FM Stellite wear products, then it is likely that the concentration of inactive Stellite constituents in the PHT water would be significantly lower than in the FM water samples.

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[1] This is a light water system similar to the HWAS and provides check-out and leak testing of the FM head and suspension before the FM is returned to service.

Each sample was supplied in two 1-L bottles. Because of normal sample preservation protocols, the collected samples were inadvertently acidified, some to pH 1 and others to pH 5 (see Tables 1 & 2). Sample collection was completed by January 17, 2008.

Table 1: Heavy Water Samples Collected from Darlington Fueling Machines

Sample #	pH of Received Sample	Facility	Sampling Point
FM1	5	Trolley 1	V10 (unfiltered)
FM2	5	Trolley 2	V10 (unfiltered)
FM3	1	Trolley 3	V10 (unfiltered)
FM4	1	Trolley 4	V10 (unfiltered)
FM5	5	Trolley 1	V11 (filtered)
FM6	5	Trolley 2	V11 (filtered)
FM7	1	Trolley 3	V11 (filtered)
FM8	1	Trolley 4	V11 (filtered)
FM9	1	Trolley 1	V10 (unfiltered)
FM10	1	Trolley 2	V10 (unfiltered)
FM11	5	Pressure Test Facility	V9 (unfiltered)
FM12	5	Pressure Test Facility	V51 (filtered)

Table 2: Heavy Water Samples Collected from Darlington PHTS

Sample #	pH of Received Sample	Sampled Loop	Timing of Sample
PHT1	5	North Loop	Coincided with collection of FM1,2,5,6 samples
PHT2	5	South Loop	Coincided with collection of FM1,2,5,6 samples
PHT3	1	North Loop	Coincided with collection of FM3,4,7,8 samples
PHT4	1	South Loop	Coincided with collection of FM3,4,7,8 samples
PHT5	1	North Loop	Coincided with collection of FM9 and FM10 samples.
PHT6	1	South Loop	Coincided with collection of FM9 and FM10 samples.

3.0 ELEMENTAL COMPOSITION OF RECEIVED WATER SAMPLES

Elemental compositions of the received water samples were determined using Induction Coupled Plasma – Mass Spectrometry (ICP-MS). The data were developed after digestion of the samples and hence represent the total of both dissolved and particulate contributions. Selected ICP-MS results for the FM and PHT water samples are shown in Table 3. The results indicate the following:

- Fe and Li levels are similar in both FM and PHT water samples indicating that both waters intermix freely. However, the presence of relatively higher levels of Co, W, Cr, Cu and Ni in the FM water indicates that the FM is a significant source for all these elements.

- In general, there appears to be no significant difference between the various results for Trolley 1 & 2 samples (FM1/FM2, FM5/FM6 and FM9/FM10) and between the various results for Trolley 3 & 4 samples (FM3/FM4 and FM7/FM8).

- The similar levels of various elements in both the filtered and unfiltered FM water samples indicate that the unfiltered samples were not collected immediately after fuel discharge/loading or a calibration run as specified, thus allowing the wear material produced from operation of the ram to be filtered out.

- The Cr/Co, W/Co and Cr/W ratios for FM1 to FM10 samples exhibited a wide range, namely, 1-18, 0.17-10 and 0.2-7.0, respectively. Values of the measured ratios bracket the corresponding values for Stellite Star J (see Table 4). In comparison, the measured Cr/Co, W/Co and Cr/W values for FM11 & FM12 are much lower than those for Stellite Star J.

4.0 CHARACTERISTICS OF PARTICULATE IN COLLECTED WATER SAMPLES

Depending on the sample, approximately 1.7 to 2.2 kg of water was successively filtered through 1.0, 0.8, 0.45, 0.2 and 0.1 μm filters. Measured data on total solids loading (total amount of particulate captured on all filters used per kg of water filtered) and size distribution of the particulate are summarized in Table 5. Note the following:

- Within experimental uncertainty, and despite the samples having been acidified to different pH values (see Table 1 for pH values), all FM and PHT water samples contained similar levels of particulate, on average approximately 3.6E-03 g/L. Note that a similar value has been previously reported for Pickering B PHT water filtered successively through 5, 1, 0.45, 0.2 μm filter sizes [Husain and Skinner 2004]. The present results conclusively indicate that the ‘unfiltered’ samples were not collected immediately after fuel discharge/loading or a calibration run as specified, thus allowing the wear material produced from the operation of the ram to be filtered out.

- The size distribution of the particulates associated with all samples (FM, PTF and PHT) was essentially uniform.

Table 6 summarizes data for elemental composition of the filtered particulates. They were obtained by digesting the filtration membranes along with the small amounts of retained solids present on them. ICP-MS results for the digested filters were corrected by subtracting results for a blank filter. Results in Table 6 indicate the following:

- The Cr/Co, W/Co and Cr/W ratios for FM1 to FM10 samples ranged between 0.6-71, 1.5 to >15 and <0.33 to 48, respectively. The significant spread in the measured ratios is likely due to the uncertainty in the measured ICP-MS concentrations arising from the small amounts of solids available for analysis and also from uncertainty introduced as a result of acidification of the samples.

- The measured values for Cr/W bracket those for Stellite Star J. However, values for Cr/Co and W/Co generally exceeded the corresponding values for Stellite Star J.

Table 3: Elemental Composition of Received Water Samples

Sample No.	**Facility**	**Sample Point**	**Elemental Concentration (µg per g of Received Sample)**							**Ratio of Elements**		
			Co	**Cr**	**W**	**Cu**	**Fe**	**Li**	**Ni**	**Cr/Co**	**W/Co**	**Cr/W**
FM1	T1	V10	6.0E-03	7.0E-03	1.0E-03	2.0E-03	1.5E-02	3.5E-01	4.0E-03	1.2E+00	1.7E-01	7.0E+00
FM2	T2	V10	2.0E-04	2.0E-03	1.0E-03	4.0E-03	1.2E-02	3.4E-01	7.0E-04	1.0E+01	5.0E+00	2.0E+00
FM3	T3	V10	2.0E-04	1.0E-03	1.0E-03	5.0E-03	8.0E-03	3.0E-01	9.0E-04	5.0E+00	5.0E+00	1.0E+00
FM4	T4	V10	5.0E-04	9.0E-03	2.0E-03	4.0E-03	1.2E-02	3.0E-01	9.0E-04	1.8E+01	4.0E+00	4.5E+00
FM5	T1	V11	5.0E-03	5.0E-03	1.0E-03	9.0E-04	2.0E-03	3.4E-01	4.0E-03	1.0E+00	2.0E-01	5.0E+00
FM6	T2	V11	1.0E-04	5.0E-04	1.0E-03	8.0E-04	<0.001	3.4E-01	6.0E-04	5.0E+00	1.0E+01	5.0E-01
FM7	T3	V11	2.0E-04	2.0E-04	1.0E-03	5.0E-04	<0.001	2.9E-01	2.0E-04	1.0E+00	5.0E+00	2.0E-01
FM8	T4	V11	5.0E-04	7.0E-03	2.0E-03	9.0E-04	2.0E-03	3.0E-01	9.0E-04	1.4E+01	4.0E+00	3.5E+00
FM9	T1	V10	8.0E-04	1.3E-02	3.0E-03	1.1E-02	7.2E-02	3.1E-01	5.0E-03	1.6E+01	3.8E+00	4.3E+00
FM10	T2	V10	3.0E-04	5.0E-03	3.0E-03	1.0E-02	3.2E-02	3.0E-01	2.0E-03	1.7E+01	1.0E+01	1.7E+00
PHT1	-	-	<1E-04	<1E-04	<1E-04	<1E-04	1.0E-03	3.3E-01	1.0E-04	-	-	-
PHT2	-	-	<1E-04	<1E-04	<1E-04	<1E-04	2.0E-03	3.3E-01	<1E-04	-	-	-
PHT3	-	-	<1E-04	<1E-04	<1E-04	1.0E-04	2.7E-02	2.8E-01	2.0E-04	-	-	-
PHT4	-	-	<1E-04	<1E-04	<1E-04	1.0E-04	1.7E-02	3.0E-01	1.0E-04	-	-	-
PHT5	-	-	<1E-04	<1E-04	<1E-04	<1E-04	6.0E-03	2.9E-01	<1E-04	-	-	-
PHT6	-	-	<1E-04	<1E-04	<1E-04	1.0E-04	2.3E-02	3.0E-01	1.0E-04	-	-	-
FM11	PTF	V9	4.2E-02	9.0E-04	2.0E-03	3.0E-02	1.2E-02	7.4E-02	6.1E-01	2.1E-02	4.8E-02	4.5E-01
FM12	PTF	V51	4.3E-02	1.0E-04	2.0E-03	3.0E-02	5.0E-03	7.3E-02	6.2E-01	2.3E-03	4.7E-02	5.0E-02

Table 4: Stellite Star J – Values for Various Element Ratios

Element Ratio	**Value**
Cr/Co	0.86
W/Co	0.44
Cr/W	1.9

Table 5: Solids Loading and Particle Size Distribution of Fueling Machine and PHT System Particulates

Sample Description	**Solids Loading (g/L)**	**Size Distribution (wt fraction)**				
		>1.0 µm	**1.0- 0.8 µm**	**0.8-0.4 µm**	**0.4-0.2 µm**	**0.2- 0.1 µm**
Unfiltered FM water	3.0E-03 (20%)	0.22 (30%)	0.20 (56%)	0.25 (38%)	0.18 (20%)	0.16 (68%)
Filtered FM water	4.4E-03 (32%)	0.18 (25%)	0.17 (11%)	0.17 (22%)	0.14 (11%)	0.33 (31%)
PTF water	2.8E-03 (4%)	0.23 (26%)	0.20 (22%)	0.22 (10%)	0.17 (14%)	0.18 (10%)
All FM water	4.0E-03 (13%)	0.21 (0.6%)	0.19 (31%)	0.21 (0.5%)	0.16 (39%)	0.23 (1.5%)
PHT water	3.8E-03 (28%)	0.19 (23%)	0.21 (35%)	0.19 (32%)	0.19 (22%)	0.21 (52%)

Note: Data in brackets represent values for Standard Deviation/Mean x 100

Table 6: Elemental Composition of Filtered Fueling Machine Particulates

Sample No.	**Elemental Composition (µg per g Particulates)**							**Element Ratios**		
	Li	**Co**	**Cr**	**Fe**	**Ni**	**W**	**Cu**	**Cr/Co**	**W/Co**	**Cr/W**
Results for 1.0 µm Filter										
FM4	9.9E-02	5.7E-02	4.1E+00	2.5E+01	<0.25	8.5E-02	8.18E-01	7.1E+01	1.5E+00	4.8E+01
FM7	<0.025	<2.5E-02	<2.5E-02	<2.5E-02	<2.5E-01	7.6E-02	2.30E-02	-	>3.1E+00	<3.3E-01
FM8	3.9E-01	4.2E-02	<2.5E-02	<2.5E-02	<2.5E-01	6.5E-02	7.30E-02	<6.0E-01	1.6E+00	<3.8E-01
Results for 0.8 µm Filter										
FM6	1.7E-01	<2.0E-02	2.2E-01	4.7E+00	<2.0E+00	6.4E-02	6.17E-02	>1.1E+01	>3.2E+00	3.4E+00
FM11	1.6E-01	<2.0E-02	7.5E-02	1.4E+00	<2.0E+00	2.4E-02	5.18E-02	>3.7E+00	>1.2E+00	3.1E+00
FM12	1.3E-01	<2.0E-02	5.9E-02	2.3E+00	<2.0E+00	8.1E-02	<2.0E-02	>3.0E+00	>4.1E+00	7.3E-01
Results for 0.4 µm Filter										
FM4	7.0E-01	<2.0E-02	2.5E-01	8.8E-01	<2.0E+00	3.0E-01	2.49E-02	>1.3E+01	>1.5E+01	8.3E-01
FM7	2.0E-01	<2.0E-02	4.7E-02	1.5E+00	<2.0E+00	a	<2.0E-02	>2.4E+00	a	a
FM11	1.6E-01	<2.0E-02	5.5E-02	2.0E+00	<2.0E+00	1.9E-02	<2.0E-02	>2.8E+00	>9.5E-01	2.9E+00
Results for 0.2 µm Filter										
FM3	3.0E-02	<2.5E-02	<2.5E-02	<2.5E-02	<2.5E-01	8.5E-02	3.60E-02	-	>3.4E+00	<2.9E-01
FM8	3.3E-01	<2.0E-02	5.0E-02	2.1E+00	<2.0E+00	2.2E-02	<2.0E-02	>2.5E+00	>1.1E+00	2.3E+00
FM11	6.4E-02	<2.0E-02	a	1.4E+00	<2.0E+00	7.2E-02	<2.0E-02	a	.3.6E+00	a
Results for 0.1 µm Filter										
FM5	1.4E-01	<2.0E-02	1.8E-01	4.6E+00	<2.0E+00	2.2E-01	3.19E-02	>8.9E+00	>1.1E+01	8.0E-01
FM6	5.3E-01	<2.0E-02	a	3.1E+00	<2.0E+00	2.9E-01	4.98E-02	a	>1.4E+01	-4.2E-02
FM12	9.3E-02	<2.0E-02	3.7E-02	1.9E+00	<2.0E+00	1.7E-01	<2.0E-02	>1.9E+00	>8.4E+00	2.2E-01

a Measured value for sample was comparable to that for blank filter.

5.0 CHARACTERISTICS OF DISSOLVED SOLIDS PRESENT IN COLLECTED WATER SAMPLES

Selected pH 5, FM water samples which had previously been filtered through 0.1 µm filters were equilibrated with NRW37LiLC mixed bed ion exchange resins[2] to determine the contribution of dissolved ionic cobalt present. For this purpose, 500 mL filtrate was mixed with 5 mL resin for 24 hours using a magnetic stir plate. The resin was filtered out and acid stripped for analyses using ICP-MS.

Figure 2 shows the observed (β, γ) dose rate changes for a number of samples as they were first filtered and then ion exchanged. While most of the dose rate changes reflect the removal of activity via filtration and ion exchange, some of the observed changes are also attributable to radioactive decay over the measurement period. The dose rate registered on the ion exchange resins following equilibration with the water samples, along with the accompanying decrease in the dose rate for the treated water, clearly demonstrated the pick-up of significant solution activity by the IX resins. By inference, dissolved inactive Stellite wear products would also have been ion exchanged on to the resin surfaces. Note that observed dose rate changes associated with the PTF samples FM11 and FM12 were small because of the relatively low activity levels in the original samples.

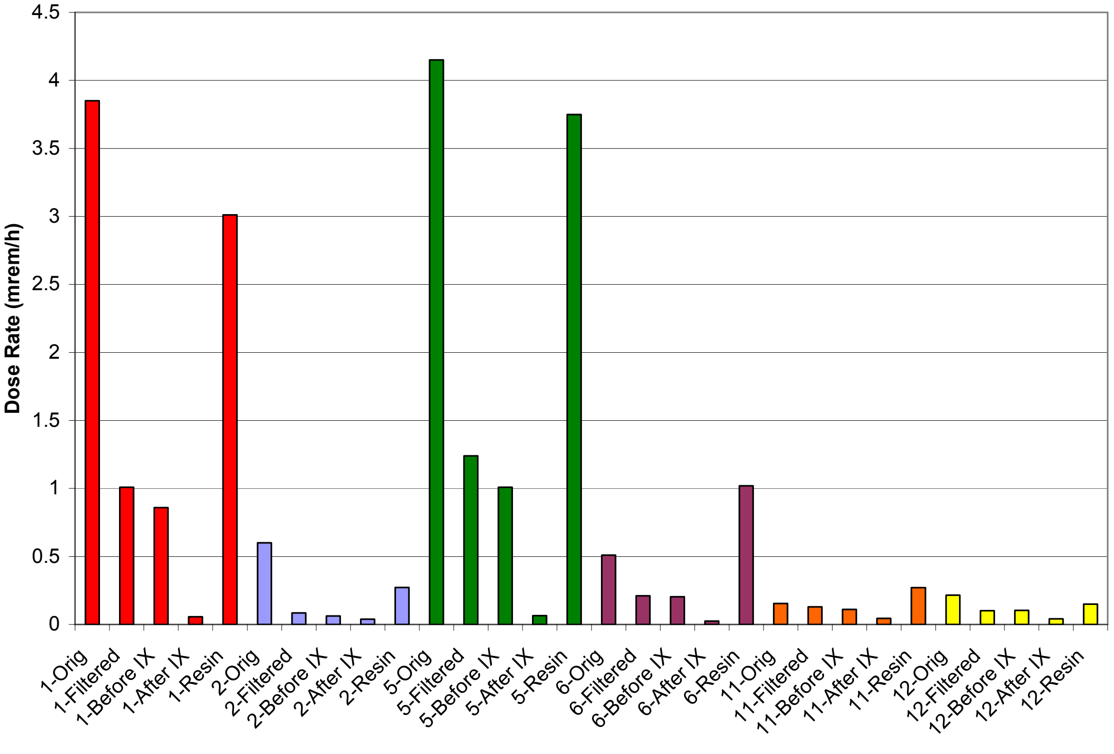

Figure 2: Variation in Dose Rates Observed During Filtration and Ion Exchange of Selected FM Samples

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[2] Both Co and Cr will be dominantly removed on cation resins under normal reducing conditions. However, under oxidizing conditions, Cr will also exist as anionic Cr(VI); hence mixed bed resins are required for clean-up.

The equilibrated resins were acid stripped to determine the elemental composition of the ion exchanged species. Results for elements of interest are summarized in Table 7. All results, with the exception of those for Ni, are relatively consistent. The observed Cr/Co, W/Co and Cr/W ratios ranged between 0.031-0.41, 0.04-0.27, and 0.63 -2.0, respectively. Unlike the measured Cr/Co and W/Co values for the filtered particulates, which generally exceeded the corresponding values for Stellite Star J (see Section 4), the Cr/Co and W/Co values measured for the exposed ion exchange resins were generally lower than the values for Stellite Star J.

Values for Cr/Co, W/Co and Cr/W ratios in Table 8 which are based on IX of the filtrates should be comparable to the corresponding values in Table 3 which are based on the 'as received' samples considering that the particulate contribution is relatively insignificant. Comparison indicates the two data sets to be consistent within a factor of 2-3 generally.

Table 7: Elemental Compositions Based on Stripping of Mixed Bed Resins*

Sample No.	Elemental Composition (µg per g Resin)						
	Li	Co	Cr	Fe	Ni	W	Cu
FM1	7.9E+03	1.1E+00	4.5E-01	7.2E+00	9.7E-01	3.0E-01	1.9E+00
FM2	7.0E+03	2.7E-02	2.7E-01	1.6E+01	1.3E+00	1.4E-01	1.8E+00
FM5	7.8E+03	9.8E-01	3.5E-01	7.7E+00	1.7E+00	1.8E-01	2.3E-01
FM6	6.3E+03	4.0E-02	2.5E-01	1.5E+01	7.6E-01	3.6E-01	7.6E-01
FM11	8.3E+03	5.2E+00	2.0E-01	9.4E+00	7.6E+01	2.1E-01	6.1E+00
FM12	8.5E+03	4.3E+00	1.3E-01	1.1E+01	6.6E+01	2.1E-01	3.5E+00

*Equilibrated with Fueling Machine Filtrates

Table 8: Elemental Ratios Based on Stripping of Mixed Bed Resins

Sample No.	Element Ratios		
	Cr/Co	W/Co	Cr/W
FM1	4.1E-01	2.7E-01	1.5E+00
FM2	9.8E+00	5.3E+00	1.9E+00
FM5	3.6E-01	1.8E-01	2.0E+00
FM6	6.3E+00	9.1E+00	6.9E-01
FM11	3.9E-02	4.0E-02	9.6E-01
FM12	3.1E-02	4.9E-02	6.3E-01

6.0 OVERALL ASSESSMENT OF DATA FOR COLLECTED WATER SAMPLES

Table 9 presents an overall assessment of the distribution of key elements between the particulate and dissolved states in the original 'as received' samples. Values for the dissolved state are represented by results for the equilibrated ion exchange resins.

Table 9: Overall Mass Balance for Key Elements of Interest

	Co	Cr	Cu	Ni	W
Results for Sample FM1					
Wt (g) in As Received Sample (A)	1.0E-05	1.2E-05	3.5E-06	6.9E-06	1.7E-06
Wt (g) associated with particulates [a] (B)					
Wt (g) associated with dissolved solids [b] (C)	1.2E-05	4.9E-06	2.0E-05	1.1E-05	3.3E-06
Total D = B+C	1.2E-05	4.9E-06	2.0E-05	1.1E-05	3.3E-06
Mass Balance: D/A	1.2	0.4	5.8	1.5	1.9
Results for Sample FM2					
Wt (g) in As Received Sample (A)	4.5E-07	4.5E-06	9.0E-06	1.6E-06	2.2E-06
Wt (g) associated with particulates [a] (B)					
Wt (g) associated with dissolved solids [b] (C)	3.8E-07	3.7E-06	2.5E-05	1.8E-05	2.0E-06
Total D = B+C	3.8E-07	3.7E-06	2.5E-05	1.8E-05	2.0E-06
Mass Balance: D/A	0.9	0.8	2.8	11.4	0.9
Results for Sample FM5					
Wt (g) in As Received Sample (A)	1.1E-05	1.1E-05	1.9E-06	8.4E-06	2.1E-06
Wt (g) associated with particulates [a] (B)	6.2E-11	5.5E-10	9.9E-11	6.2E-09	6.9E-10
Wt (g) associated with dissolved solids [b] (C)	1.3E-05	4.6E-06	3.1E-06	2.2E-05	2.3E-06
Total D = B+C	1.3E-05	4.6E-06	3.1E-06	2.2E-05	2.3E-06
Mass Balance: D/A	1.2	0.4	1.6	2.7	1.1
Results for Sample FM11					
Wt (g) in As Received Sample (A)	8.0E-05	1.7E-06	5.7E-05	1.2E-03	3.8E-06
Wt (g) associated with particulates [a] (B)	9.8E-11	1.3E-10	1.4E-10	9.8E-09	2.0E-10
Wt (g) associated with dissolved solids [b] (C)	6.2E-05	2.4E-06	7.2E-05	9.1E-04	2.5E-06
Total D = B+C	6.2E-05	2.4E-06	7.2E-05	9.1E-04	2.5E-06
Mass Balance: D/A	0.8	1.4	1.3	0.8	0.7
Results for Sample FM12					
Wt (g) in As Received Sample (A)	7.7E-05	1.8E-07	5.4E-05	1.1E-03	3.6E-06
Wt (g) associated with particulates [a] (B)	5.6E-11	1.4E-10	5.6E-11	5.6E-09	3.3E-10
Wt (g) associated with dissolved solids [b] (C)	4.9E-05	1.5E-06	3.9E-05	7.5E-04	2.4E-06
Total D = B+C	4.9E-05	1.5E-06	3.9E-05	7.5E-04	2.4E-06
Mass Balance: D/A	0.6	8.3	0.7	0.7	0.7

a Based on measured concentration and total weight of sample
b Based on measured concentration on equilibrated IX resins and total weight of sample

- In general, for all the elements shown, which include the three Stellite constituents Co, W and Cr, the dissolved contribution overwhelmingly exceeded the particulate contribution.

- Theoretically, with excess ion exchange capacity, the ratio D/A in Table 9 should be unity. Considering experimental and analytical uncertainties, D/A values for Co and W were generally about unity or lower.

- D/A values for Cr, Ni and Cu are more variable with some values (particularly those for Cu) substantially and inexplicably exceeding unity. These anomalies may have resulted from cross-contamination between samples during filtration.

Despite the anomalies, the results clearly indicate the benefits of using ion exchange media for removing dissolved ram ball wear products present in the FM water.

5.0 CHARACTERIZATION BASED ON FILTER AND SMEAR SAMPLES - ESTIMATION OF RAM BALLS WEAR RATE

In addition to providing water samples, Darlington also provided smear samples from FM filter housings and dose rate data for the spent filters during two recent filter change-outs. Dose rate data for a spent FM filter and a cut-out of the spent filter material (see Figure 3) were also available from a previous project. Table 10 summarizes data for the three spent filters.

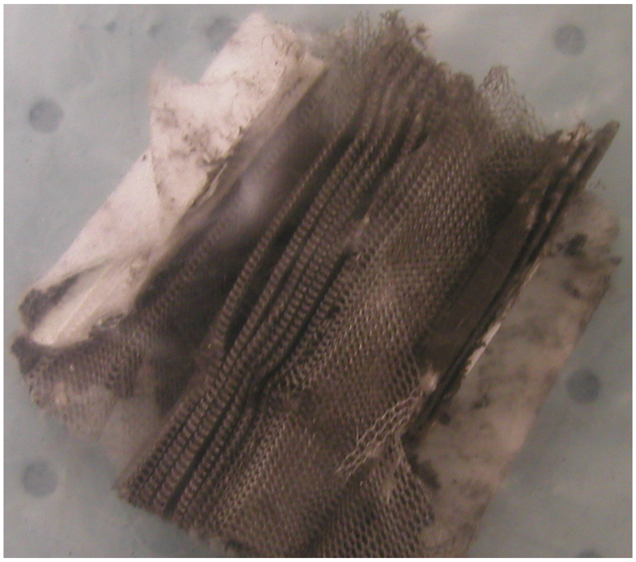

Figure 3: Sample of a Fueling Machine Filter Material

Table 10: Particulars of FM Filter Samples and Dose Rate Data

	Trolley 3 / 4	Trolley 1	Trolley 2
	May 31, 2006	**Sept 25, 2007**	**Sept 25, 2007**
Dose rate (mrem/h) above filter located inside vessel (lid of vessel removed)	120 mrem/h @60 cm		
Dose rate (mrem/h) above filter (removed from vessel)	1500 mrem/h @30 cm	400 mrem/h @10 cm	300 mrem/h @10 cm
Dose rate (mrem/h) at side of filter (removed from vessel)	1300 mrem/h @30 cm	1.9 rem/h @10 cm 800 mrem/h @ 30 cm	1.3 rem/h @ 10 cm 260 mrem/h @30 cm
Dose rate (mrem/h) at bottom of filter (removed from vessel)	-	2 rem/h @ 10 cm	1 rem/h @ 10 cm
Sample taken	Filter material	One smear from filter housing lid and one from side walls of filter housing	One smear from filter housing lid and one from side walls of filter housing

The samples and dose rate data were utilized as follows to determine the accumulation rate of inactive Co-59 on the filters during operation:

- The smear and filter samples were gamma scanned to determine their fractional radionuclide activity distributions. These along with the measured spent filter dose rate data yielded estimates for the total spent filter Co-60 activities.
- Measurement of the Co-59 elemental contents of the smear paper/filter cut out along with their Co-60 activities yielded estimates for Co-59/Co-60 ratios.
- The total inventory of Co-59 on the spent filters was determined from the overall spent filter Co-60 activity and the Co-59/Co-60 ratio.
- The average Co-59 accumulation rate on a spent filter was calculated from the estimated Co-59 inventory considering that a filter is typically replaced after about 3 months.

Measured Co-59/Co-60 ratios and estimated Co-60 and Co-59 spent filter inventories are shown in Table 11. As shown, the yearly Co-59 accumulation rate on a spent filter was estimated to range between 8 and 30 g. Assuming the contribution of Co-59 in sub-micron particulate (pore size of filter is 1 um) and in soluble form to be relatively small, the estimated Co-59 accumulation rate also represents the release rate of Co-59 from ram ball wear on a trolley. Note that the lower value of 7.6 g/year estimated thus is consistent with a reported estimate of 6 g per year for Gentilly-2 fueling machine [Gauthier and Guzonas 2007].

An estimate of the total solids loading per filter was obtained using the estimated Co-59 inventory in Table 11 and the measured elemental composition data for the particulates (see Table 6). The amounts estimated thus ranged up to 466 g, consistent with the maximum filter holding capacity of approximately 900 g [Walker 2005] thus providing an additional measure of validity for the calculations presented here.

Table 11: Estimated Co-59 Inventory and Accumulation Rate on Spent Filters

Filter	Co-60 (Bq)	Co-59/Co-60 (µg/Bq)	Co-59 Inventory (g)	Accumulation Rate of Co-59 on Spent Filters (g/year per Trolley)	Solids Loading of Spent Filter (g)
Trolley 3/4	2.2E+08	8.8E-03	1.9	7.6	80
Trolley 1	1.1E+09	6.9E-03	7.6	30.4	365
Trolley 2	7.4E+08	8.0E-03	5.9	23.6	466

Assuming that the estimated Co-59 inventories originated entirely from the Stellite Star-J material in the Darlington FMs, estimates for the ram balls wear rate were obtained as shown in Table 12. The results indicate that the wear rate varies significantly between various FM rams. These estimates should be rationalized by comparison with direct estimates based on the measured reduction in diameter of ram balls. Currently, there are no direct measurement data for ram ball wear rates at Darlington.

Table 12: Estimated Ram Balls Wear Rate

Filter	Ram Balls Wear Rate* (g/y)
Trolley 3/4	22
Trolley 1	84
Trolley 2	66

*Wear rate (g/y) = Co-59 Inventory (g)/36%/(3 mo/12 mo/y)

A comparison of the relative ratios of measured Co, Cr and W in the filter/smear samples with the corresponding ratios for Stellite Star J is shown in Table 13. The measured W/Co ratios are reasonably constant but lower than the corresponding value for Stellite Star J. On the other hand, the Cr/Co and Cr/W ratios are more variable and generally higher than the corresponding values for Stellite Star J.

Table 13: Relative Ratios of Cobalt, Chromium and Tungsten in FM Filter/Smear Samples

	Cr/Co	W/Co	Cr/W
Trolley 3/4 filter sample	8.9E-01	1.4E-01	6.2E+00
Trolley 1 smear sample[a]	9.0E+00	1.5E-01	6.1E+01
Trolley 1 smear sample[b]	1.8E+00	1.0E-01	1.8E+01
Trolley 2 smear sample[a]	3.1E+00	1.7E-01	1.8E+01
Trolley 2 smear sample[b]	3.2E+00	1.6E-01	2.0E+01
Stellite Star J	**8.6E-01**	**4.4E-01**	**1.9E+00**

a smear from filter housing lid
b smear from side walls of filter

6.0 DISCUSSIONS

Cobalt may be released from Stellites by a combination of wear and corrosion. While corrosion would be insignificant at typical FM water temperatures of about 60ºC, it would be important at the much higher operating temperatures which occur transiently. At elevated temperatures and under reducing conditions in lithiated water, a thin protective surface oxide film is formed which is strongly enriched in Cr due to preferential dissolution of Co and W [Guzonas 2007]. Under mildly oxidizing conditions (internal FM components are exposed to transient oxidizing conditions during some modes of operation), Cr also may be released as a result of Cr (III) oxidation to Cr(VI).

Subsequent wear of the oxidized surfaces will result in the removal of Co depleted surface oxide film and hence the introduction of wear particles into the water consisting of the surface film oxidation products such as CoO, Cr_2O_3, $Cr(OH)_3$, Co_2O_3, $CoCr_2O_4$, NiO, $NiCr_2O_4$, WO_3 and WO_2 [Guzonas 2007]. Subsequently, the Co containing wear particles could also undergo corrosion and release dissolved Co species.

Table 14 summarises measured values for the elemental ratios Cr/Co, W/Co, and Cr/W. Considering that Co and W are preferentially dissolved, one expects their dissolved concentrations to be higher than expected based on the composition of Stellite Star-J. On the other hand, preferential dissolution of Co and W will cause the particulates to be depleted in these elements. The results shown in Table 14 are consistent with this expectation, i.e., for both Cr/Co and Cr/W

$R_{\text{particulate}} > R_{\text{Stellite Star-J}} > R_{\text{Dissolved}}$

where R denotes either elemental ratio.

Table 14: Summary of Measured Values for Elemental Ratios Cr/Co, W/Co and Cr/W

	Cr/Co	W/Co	Cr/W
Particulate wear products (data from Table 13)	0.9-9.0	0.1-0.17	6-61
Dissolved wear products (data from Table 8)	0.031-0.41	0.04 – 0.27	0.63 -2.0
Stellite Star J	**8.6E-01**	**4.4E-01**	**1.9E+00**

7.0 CONCLUSIONS AND RECOMMENDATIONS

- Circulating water in the HWAS which has been filtered through a 1 μm filter contains a particulate loading of approximately 3.6E-03 g/L similar to that present in the PHT water. The particulate has a relatively uniform size distribution in the range 1.0-0.1μm. The presence of Co, W and Cr present in the particulate originates from wear of the FM ram balls.

- In the absence of particulate loading data for unfiltered water in the HWAS, it was not possible to directly assess the merits of replacing the current filter size with a 0.1 μm filter. In addition to the presence of sub-micron particulate, the filtered FM water also contained dissolved constituents with the dissolved Co, W and Cr bearing a signature of ram balls wear product. The dissolved Co, W and Cr content was overwhelmingly greater than that associated with the sub-micron particulate.

Therefore, installation of a mixed bed ion exchange column in the HWAS appears to be very beneficial and is, therefore, recommended.

- Spent 1 µm fueling machine filters were estimated to contain 2-8 g of inactive Co-59. Assuming the contribution of Co-59 in dissolved and submicron particulate to be relatively small and a filter replacement frequency of 3 months, the estimated Co-59 filter inventory represents a ram balls wear rate of 22-84 g/year for each fueling machine. Darlington does not currently measure ram balls wear rates and, therefore, the values estimated here cannot be independently confirmed.

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- It would be useful to develop FM ram balls wear rates data based on analysis of smears and dose rate data for Pickering spent FM filters. Estimated FM ram balls wear rates obtained from this data can be compared with directly measured Pickering wear rates data. If validated, the technique may provide a simple and less dose intensive means for measuring ram balls wear rates.

- An assessment of the relative contribution of fueling machines to the PHT Co-60 source term must be carried out. Fueling machine water is introduced into the PHTS during on-power channel operations. Such an analysis would be particularly important to support the possible replacement of the ram balls material.

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