PRIMARY SIDE CRUD SAMPLING AND CHARACTERIZATION:

HOW IT MAY HELP TO BETTER MAINTAIN CANDU REACTORS

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Abstract

The paper reports a corrosion-product transport study in the primary-side of CANDU reactors. The study is based on systematic crud sampling examinations at Darlington NGS. Emphasis is placed on the corrosion-product transport and oxidation state as a monitor of primary water chemistry state, and as a monitor of system corrosion effects. The D_2O was sampled at reactor outlet headers and the deposits collected on 0.45 μm membrane filters were analyzed by using γ-ray spectroscopy, X-ray fluorescence and Mössbauer effect techniques. In the beginning of this study in 1994 and 1995, the steady state crud concentration used to be as high as 20 to 30 μg/kg D_2O, and the crud contained large fractions of highly oxidized species (40 to 60% Fe), in the form of ferrihydrite, lepidocrocite, goethite and hematite. During start-up operations, the crud concentrations were as high as 8 mg/kg D_2O, and contained 70 to 80% Fe in the form of oxidized iron species. However, as a result of various improvements, and especially because of better oxygen control during lay-ups (nitrogen blanketing) and better pH control (lower and more stable values), in recent steady-state runs, the crud concentrations were found to be lower than 3 to 5 μg/kg D_2O. At present, the steady-state crud consists mostly of Fe, largely in the form of magnetite (60 to 80% Fe), and hematite (20 to 40% Fe). The steady-state concentration of crud was found to increase markedly with pH_a in the range from 10.3 to 10.7. This seems to be in accord with the trend predicted by flow-assisted solubility of magnetite in lithiated water at ~300°C, and is generally in accord with the model of dissolution, transport, and redeposition of iron in the primary heat transport system of CANDU reactors. The crud contains also significant amounts of Zr (~5 to 30 wt.% Fe), apparently in the form of zirconium oxide. Zirconium oxide particles may originate largely from the wear of fuel bundle pads and pressure tube fretting; which should be minimized.

1. Introduction

Regular monitoring of reactor water systems by filtration and analysis of particulate corrosion products (crud), as well as dissolved species (solubles), has become an important element of secondary-side water chemistry optimization and system surveillance in most Canadian CANDU plants [1]. Recently, crud sampling has also been investigated as a tool to assist in primary-side maintenance [2]. Primary-side crud sampling may provide useful information for improving chemistry control, extending the lifetime of fuel channels and system components, lowering activity transport and steam-generator fouling, and, possibly, for preventing outlet-feeder thinning.

Oxygen, hydrogen and pH are major concerns of any primary-side chemistry control program. In particular, a careful pH control is essential to minimize carbon steel corrosion. The current chemistry control strategy in most CANDU nuclear power stations is to add hydrogen (deuterium) to the primary coolant to ensure that oxygen is not produced radiolytically. However, adding excess hydrogen can lead to hydriding of pressure tubes. Therefore, the hydrogen addition has to be carefully optimized.

Corrosion products formed in primary coolant system indicate undesirable degradation of system components and cause a wide variety of problems, such as reduced heat transfer and radioactivity transport. The reasons

why corrosion-product transport (CPT) should be controlled and characterized are:

- it points to excessive general corrosion and, in particular, flow-accelerated corrosion (FAC) of feeder pipes;
- crud activation increases the activity transport and build-up of occupational radiation exposures;
- oxidized iron may indicate air in-leakage's; as well as not enough dissolved deuterium in water;
- CPT increases in-tube deposition and fouling of steam generators, and under-deposit corrosion;
- fouling causes flow pressure drop and increases reactor inlet header temperature (RIHT);
- it may cause the increased frequency of chemial-cleaning and volume of radwaste;
- it fouls bleed filters and purification systems;
- it deposits on pressure tubes and inlet fuel bundles; and
- overall it may increase the length of outages.

In this paper we report a PHT system study; which is being performed with the following primary objectives:

- develop procedures for sampling and analyzing tritiated D_2O with radioactive crud;
- determine crud transport and composition;
- examine effectiveness of hot conditioning;
- compare steady-state and start-up effects;
- identify main sources of crud transport and possibilities for its remediation; and
- identify the origin of oxidized iron species.

2. Technical Procedures

System Layout

The primary heat transfer system in CANDU reactors in Darlington has two loops, north and south, with water passing through the east and west boilers. As is schematically shown in Figure 1, deuterium is added in the second path (at discharge of pumps 1 and 2). Purification is done after boiler 1, but at a fairly small rate of 10 to 12 kg/s. Water is sampled at the reactor outlet headers, before entering boiler 1.

Sampling Procedure

Studies of PHT crud transport and its chemical composition in Darlington NGS were initiated in 1990 during the hot conditioning of Unit 1. In 1992, the start-up crud transport was examined after a prolonged shutdown of Unit 2 (for 1.5 years). During these studies 1 L grab samples were taken. In 1994, a procedure was developed for integrated in situ sampling during steady-state, and North and South loops in Units 1 to 4 began to be sampled sporadically [2]. Since 1996 April, the sampling of Units 1 to 4 has been performed regularly at approximately 3 months intervals.

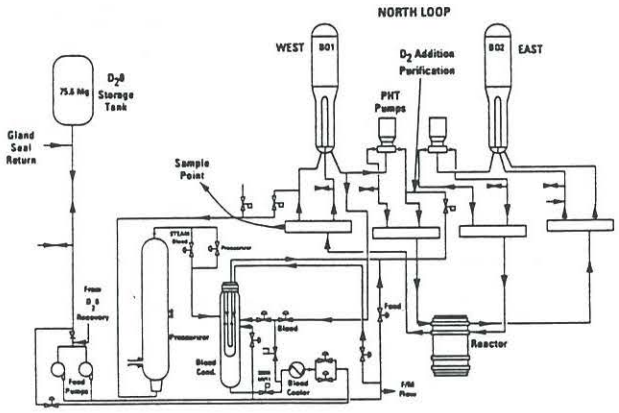

Figure 1. Simplified primary side (North loop) layout with indicated sample and D_2O addition-purification points.

The heavy water is sampled using standard sampling lines (length <20 m) leading from the reactor outlet headers to the modified integrated crud samplers installed in each of reactor water sampling rooms. Before reaching the sample holder, the water is cooled to about 50°C and depressurized. Each sampling runs typically 24 h and uses ~200 L D_2O, which is recovered.

A special procedure had to be developed to sample hot tritiated water containing substantial amounts of radioactive species without spillage and waste. It involves using a special vessel to allow D_2O to completely drain from the filter housing as described in reference [3]. Standard 0.45-μm-sized 47-mm cellulose membrane filters were used in all tests. Application of ion exchange filters is planned in the next sampling sessions to determine the solubles-to-particulates ratio.

An example of coolant chemistry parameters; pH, conductivity, deuterium, lithium, and chloride; recorded prior to crud sampling, is given in Table 1. Table 2 gives a record of sampling conditions during one of the typical sampling sessions.

Mass Gain Determination

After exposure, the filters were dried at ambient temperature for 24 h in a dessicator. Mass gain was determined by comparing the weight of the filters at the station chemical laboratory, before and after exposure to water. Recently, mass gain was typically 50 to 100

$\mu g/cm^2$. Room temperature drying may introduce a big weighing error because of remaining adsorbed water both in the micropores of the filter and crud deposits. Note that the weighing procedure for non-radioactive filters from secondary-side water is different and it involves hot drying (usually at 80°C).

Table 1. Typical record of system chemistry parameters prior to 1996 July 24 sampling.

Unit (Loop)	pH	Cond. (mS/m)	Deut. (cc/kg)	Li (mg/kg)	Cl (µg/kg)
1-N	10.34	2.12	2.31	0.76	6.3
1-S	10.34	2.09	2.50	0.73	3.3
2-N	10.35	2.04	5.15	1.04	24.5
2-S	10.35	2.04	5.93	1.05	21.9
3-N	10.41	2.14	5.51	0.99	8.1
3-S	10.41	2.13	5.32	0.99	12.7
4-N	10.39	2.14	4.94	0.98	11.4
4-S	10.39	2.16	4.53	0.98	10.7
specs.	10.3-10.7	-	3-10	-	<200

Table 2. Typical sampling conditions. 1996 July 24 session.

Unit (Loop)	γ Contact (mR/h) after 48 h	β Contact (mR/h) after 48 h	Water Vol. (L)	Wt. (mg)	Crud Conc. (µg/kg)
1-N	10	200	231	2.9	11.4
1-S	10	400	171	1.4	7.4
2-N	10	1000	268	2.0	6.8
2-S	10	1000	222	1.1	4.5
3-N	5	400	232	1.1	4.3
3-S	10	500	315	3.7	10.7
4-N	5	200	127	1.1	7.9
4-S	5	200	134	0.9	6.1

Gamma-spectroscopy

The PHT crud filters are radioactive and have to be handled very carefully. The filters contain a variety of activation products and some tritium. They may also contain small hot particles (fleas) from possible failures of fuel elements.. As seen in Table 2, typical activity per filter 48 h after sampling was ~10 mR/h in γ-contact and up to 1000 mR/h in β-contact.

Gamma-spectroscopy was used to determine the inventory of radionuclides on the filters, both at the station and at CRL laboratory. Gamma-spectra using a high-energy (>50 keV) Ge(Li) detector have shown six major radionuclides: ^{137}Cs, ^{95}Nb, ^{95}Zr, ^{124}Sb, ^{134}Cs and ^{60}Co. Corresponding activities in one of the sampling sessions are compared in Table 3, as an example. Full lists of radionuclides found are filed and are available on request.

In addition, an intrinsic Ge detector equipped with Be window was used at CRL to measure a low-energy X- and γ-rays (~3 to 50 keV). This allowed us to determine low-energy X-ray and γ-ray emitters such as ^{55}Fe and ^{119}Sn.

X-Ray Fluorescence

An X-ray fluorescence method is being optimized to determine nondestructively the elemental composition and mass of the filtered deposits. The development and applications of XRF method in filter analysis have been described in reports [4,5] and in a preceding paper [6]. The XRF method is more practical than digestive chemical methods of analysis, which have to deal with low level radioactive liquid waste produced during

Table 3. Gamma-spectroscopy record of six major radionuclides
(1996 July 24 sampling - July 31 analysis)

Unit (Loop)	Total Activity µCi	% of Total Activity						Total (%)
		^{60}Co	^{95}Nb	^{95}Zr	^{124}Sb	^{134}Cs	^{137}Cs	
1-N	0.82	7.1	27.5	15.4	14.4	3.1	8.7	76.2
1-S	1.31	1.6	16.0	9.6	1.7	3.0	8.8	40.7
2-N	6.40	0.6	8.3	5.6	20.5	6.7	20.5	62.2
2-S	6.26	0.7	6.3	4.3	12.3	7.6	23.5	54.7
3-N	3.84	1.4	13.3	15.4	9.5	7.8	19.6	63.6
3-S	4.58	3.2	23.8	9.6	20.7	5.4	13.7	83.5
4-N	1.08	1.1	9.6	7.2	6.7	5.9	18.8	49.3
4-S	1.16	1.5	12.4	9.1	5.2	5.5	17.7	51.4
$T_{1/2}$		5.3 a	35 d	64 d	60 d	2.1 a	30.2 a	

specimen analysis. The XRF is nondestructive and can be performed prior to further analysis of specimen by other methods, such as Mössbauer spectroscopy and electron microscopy. It also appears that the mass determination by the XRF technique can be more accurate than by weighing. Further, the XRF analyzer used is portable and can be used in field (quasi online) work. It is also capable of measuring low-energy γ-emitters and EC decaying radionuclides, such as ^{55}Fe.

Samples from 1996 February, 1996 December and 1997 April sampling sessions have been analyzed by XRF method. The XRF was performed using ^{108}Cd and ^{241}Am sources. Each measurement was integrated over a central area of filter of ~10 cm^2. Major elements found were Fe and Zr; a number of minor elements was also identified. Table 4 gives a typical XRF record of Fe and Zr from one of the sampling sessions

Table 4. Typical XRF record of Fe and Zr mass determination. 1997 April 2 filters.

Unit (Loop)	Fe μg/cm^2	Zr μg/cm^2	Zr/Fe Ratio	Mass Ratio weight/XRF
1-N	14.7	0.8	0.05	2.8
1-S	28.3	2.5	0.09	1.2
2-N	25.8	4.4	0.17	3.2
2-S	21.2	1.7	0.08	1.6
3-N	16.5	5.4	0.33	2.2
3-S	82.4	9.9	0.12	1.1
4-N	14.5	1.2	0.08	5.1
4-S	44.7	3.2	0.07	1.9

A summary of Fe and Zr concentrations in μg per kg D_2O (ppb) measured so far is shown in Figure 2. As can be seen, during three sampling sessions crud levels were systematically lower for Units 2 and 4. High crud levels observed in Units 1 and 2-N in 1996 February, decreased markedly during later sampling sessions. XRF data for 1997 sampling session show that in a well-controlled steady-state of reactor operation, Fe concentration can be as low as ~1 ppb and Zr concentration is at the level of 0.1 ppb. The highest concentration of Zr (up to 30 wt.% Fe) has been observed so far in Unit 3 North samples. The reason of these differences is being investigated

Scanning electron microscopy and X-ray dispersive analysis of filters showed that whileiron represented very fine ~μm-sized particles, zirconium was often present in a form of 20 to 30-μm-sized particles. It is likely that zirconium in the crud originates from Zr-2.5Nb pressure tubes oxide spalling, from axial scratch marks on the inner tube surfaces during axial motion of fuel bundles, and from fret marks at the inlet ends of the pressure tubes caused by the bearing pads, as well as it can come from fretting of Zircaloy-4 bearing pads on fuel sheathing. The mass of Zr in the crud should be correlated with these wear effects. Further systematic monitoring of Zr and evaluation of other elements in the crud should help to elucidate its main sources.

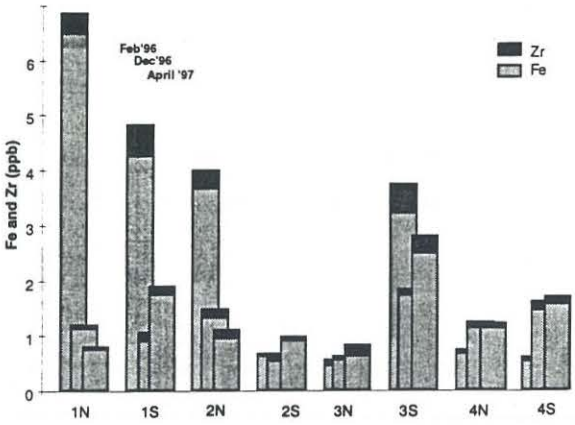

Figure 2. Concentrations of Fe and Zr in crud measured using X-ray fluorescence analysis of filter deposits obtained from 3 recent steady-state sampling sessions.

Mössbauer Spectroscopy

Mössbauer spectroscopy was used to establish the chemical form and oxidation state of iron and tin. Similarly to secondary side filter analysis [7], the transmission spectra of 14.4 keV γ-rays in ^{57}Fe are detected with a Kr-CO_2 proportional counter, but the measurements were significantly more difficult because of the radioactivity of the absorbers [8]. All ^{57}Fe spectra were obtained at room temperature using a 50 mCi ^{57}CoRh Mössbauer source.

Iron is found mostly as magnetite, Fe_3O_4, but fractions of reducible iron Fe(III) oxides and hydroxides (ferrihydrite; $Fe_5HO_8.4H_2O$, hematite; α-Fe_2O_3, maghemite; γ-Fe_2O_3, goethite; α-FeOOH, and lepidocrocite; γ-FeOOH) were also found and often were at higher concentrations than could be expected in lithiated water under reducing conditions. A summary of Mössbauer spectroscopy data for filters from one of steady-state sampling sessions is given in Table 5, as an example. The speciation of iron oxides observed and its relationship to system chemistry are discussed in Sections 3 and 4.

Using 23.9 keV γ-rays emitted by radioactive ^{119}Sn in the deposits, Mössbauer spectra of minute quantities of

tin in the filters were also measured [9]. Tin, presumably incorporated in zirconium oxide particles, was found to be in oxidized state Sn(IV), same as in stannic oxide SnO_2, and same as observed in oxide scrapes from the Zircaloy-2 pressure tube.

Table 5. Example of Mössbauer ^{57}Fe spectroscopy analysis of PHT specimens. 1996 July 24 sampling session.

Unit (Loop)	Phase Composition (wt. % Fe)			
	Fe_3O_4	α-Fe_2O_3	α-FeOOH	γ-FeOOH
1-N	81±2	16±1	--	3±1
1-S	82±2	14±2	--	4±1
2-N	81±1	--	--	19±1
2-S	48±2	15±7	--	37±1
3-N	41±2	--	6±1	53±1
3-S	68±1	--	--	32±1
4-N	35±2	--	--	65±2
4-S	47±1	--	--	53±1

3. Chemical Form of Iron

The chemical form of iron in the crud and its oxidation state provide an insight into its origin and PHT chemistry.

Hot Conditioning

Before entering into service, Units 1 and 2 were hot-conditioned with EDTA and Units 3 and 4 with NH_3, N_2H_4 and some Li(OH). During hot conditioning with lithiated light water, EDTA and 25 ppm N_2H_4 were added at the beginning of the cycle.

The set of 15 archived filters from Unit 1 EDTA conditioning in 1990 was examined in 1995. During conditioning, the system was kept at 145°C for 6 h and then at 250°C for 36 h. The evolution of Fe species obtained from Mössbauer spectra is plotted in Figure 3 (top) as a function of the time. As seen, at 145°C, ferric oxyhydroxides (α- and γ-FeOOH) have quickly (~12 h) converted to almost totally magnetite (~90%), indicating quick conversion (after 12 h) to a desirable so-called black state. The iron transport shows a rather complex behavior, but it reaches low values (fraction of ppm) at the end of the conditioning cycle. Figure 3 (bottom) shows, that in this case, the crud transport data obtained by weighing and from evaluation of the Mössbauer spectra were quite consistent.

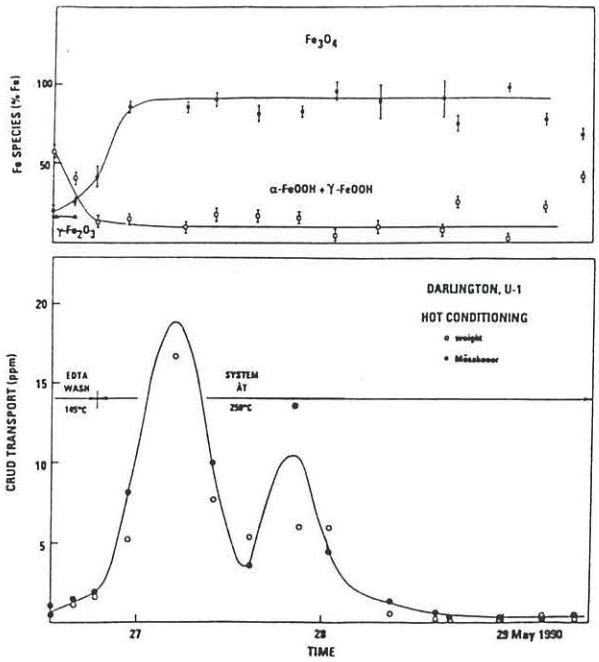

Figure 3. Results of DNGS Unit 1 hot conditioning in 1990. Top: evolution of iron species with time. Bottom: crud transport as determined from mass gain of filters and from Mössbauer spectra.

Cold Lay-ups and Preconditioning

During cold lay-ups and preconditioning, considerable amounts of ferrihydrite was found in the large D_2O storage tank (TK1), in addition to hematite and maghemite. Ferrihydrite deposits were also observed on the end-shield carbon steel plugs in pressure tubes after prolonged lay-up (1.5 a) of Unit 2. The formation of ferrihydrite usually occurs by the oxidation of Fe^{2+} in the presence of crystallization inhibitors, such as organics, phosphate and silicate species. Phosphates have been observed in primary side, for instance in Bruce A pressurizer heater. Ferrihydrite is thermodynamically unstable and with time transforms into goethite, hematite, or mixture of the two.

Start-ups

During reactor warm-ups and start-ups iron was found mostly observed in the form of ferrihydrite and goethite. Measurements were performed for Unit 2 in 1992 and Unit 4 in 1994. Start-up crud concentrations were as high as 3 ppm and 8 ppm, respectively (see Figure 4). The magnetite fraction increased slowly with time in the early operational phase.

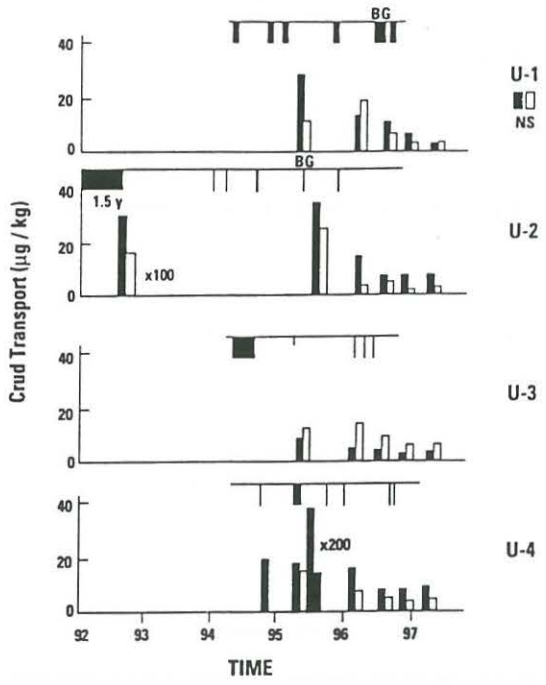

Figure 4. PHT crud concentration in DNGS Units 1 to 4 as a function of time; in all cases crud mass was determined by weighing. N and S stand for North and South loops, respectively. Major outages and shutdowns are depicted above each plot. BG indicates start of applications of N_2 blanketing gas.

Steady-state

The fractions of magnetite during steady-state reactor operation varied widely between 50 and 80% (in %Fe) in Unit 1, 30 to 95% in Unit 2, 45 to 70% in Unit 3 North, and 30 to 70% in Unit 4 (see Figure 5). The balance is lepidocrocite, goethite and hematite. Note that 100% magnetite is commonly expected and assumed in the heat-transfer models.

Generally, the fraction of magnetite increased between 1994 and 1997 (see Figure 5), suggesting that more and increasingly reducing conditions were slowly established in the system. This is consistent with loop experiments by Allsop et al. [10], which have shown that the conversion of iron oxides in lithiated water, and especially reduction of hematite to magnetite in CANDU primary coolant, is very slow and may take several weeks to convert to stable oxide form.

Since 1996 February, the N_2 gas blanket has been used during outages, and the samples showed an absence of lepidocrocite in Units 3 and 4, and very little in Units 1 and 2. There was also no goethite in Units 1 and 3. Because goethite and lepidocrocite should be unstable at PHT temperatures, their presence in the filters would indicate the ingress of these oxidized iron species into the circuit from low-temperature components of the system, such as purifiers, storage tanks, fueling machines, etc.

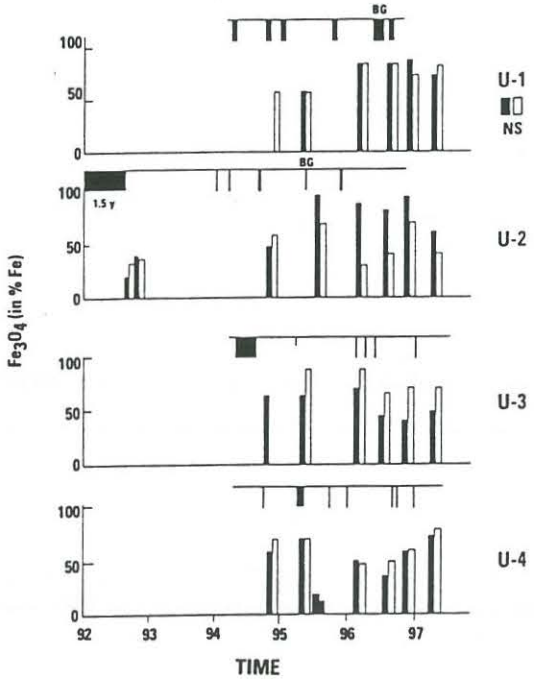

Figure 5. Fractions of magnetite in PHT filter deposits recorded during various sampling sessions. The balance of iron is made up of iron (III) oxides and oxyhydroxides.

It is to be noted that at present the steady-state composition of iron oxides in DNGS PHT crud is quite comparable to the secondary-side blowdown crud composition.

4. Discussion of Results

Effects of Primary-Side Chemistry

An analysis of PHT crud transport at DNGS Units 1 to 4, North and South loops indicated that there may be a correlation between the concentration of crud and the pH_a of heavy water [11]. An updated and more complete correlation is shown in Figure 6. The pH_a values in Figure 6 are in most cases reported as averaged values over a 4-week period prior to sampling; in cases when pH_a in this period varied more than 0.2 units (mostly prior to 1994 and 1995 samplings), the average values for 2 to 5 days before sampling were accepted.

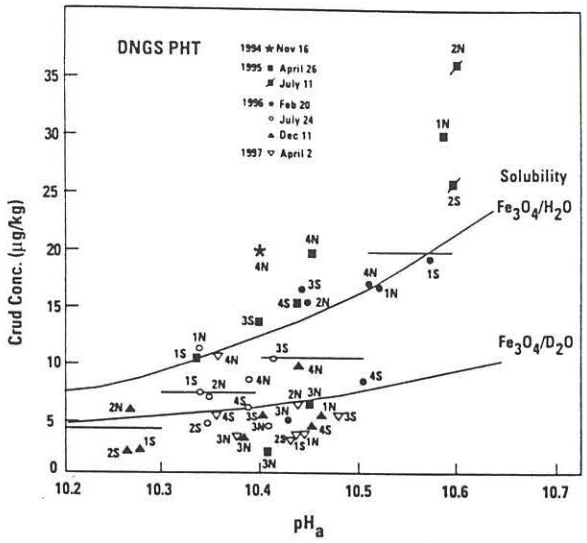

Figure 6. Crud concentration in DNGS PHT system as a function of pH_a. The sampling dates are indicated in the legend. Crud mass was determined by weighing. Solid lines indicate solubility of magnetite in lithiated water at 310°C calculated by E. Cheluget according to Sweeton and Baes model.

The horizontal bars represent the average value of data points in 0.1 pH_a intervals. As seen, the average crud concentration increases from ~4 μg/kg at pH_a = 10.2 to 10.3 to about 17 μg/kg at pH_a = 10.5 to 10.6. The crud level rises quickly beyond pH_a > 10.5. Recently, at pH_a of 10.4 to 10.5, the concentrations of filterable species in PHT in Darlington were comparable to the secondary-side crud concentrations.

The continuous lines in Figure 6 indicate the solubility of magnetite in lithiated H_2O and D_2O at 310°C, as a function of pH_a, which were calculated by E. Cheluget using Sweeton and Baes thermodynamic data [12]. Although there is much scatter in the data, the experimental points support the trend predicted by solubility of magnetite in lithiated water at 310°C. This is generally in accord with the current model of dissolution, transport, and redeposition of iron in the primary heat transfer system of CANDU reactors offered by Burrill and Cheluget [13,14].

Based on these observations, one may postulate that lowering the pH_a towards the lower end of current DNGS specifications (10.3 to 10.7) would help to decrease the solubility of magnetite and thus lower crud generation and transport. This may help in alleviating the feeder thinning, RIHT, and activity transport. In fact, in 1997 July, based the new PHT chemistry guidelines issued by AECL [15], DNGS decreased the PHT pH_a to the 10.1 to 10.4 range. On the other hand, as suggested by Burrill [16], at low pH more crud may be deposited in core and irradiated, and hence operation at low pH range may result in higher activity transport. The filters that have been taken at this new pH_a range (at 50% power) and will be soon analyzed.

Other correlations of the DNGS data are not evident. In particular, Figure 7 shows that there is no apparent correlation between crud concentration or fractions of magnetite and dissolved deuterium in PHT water.

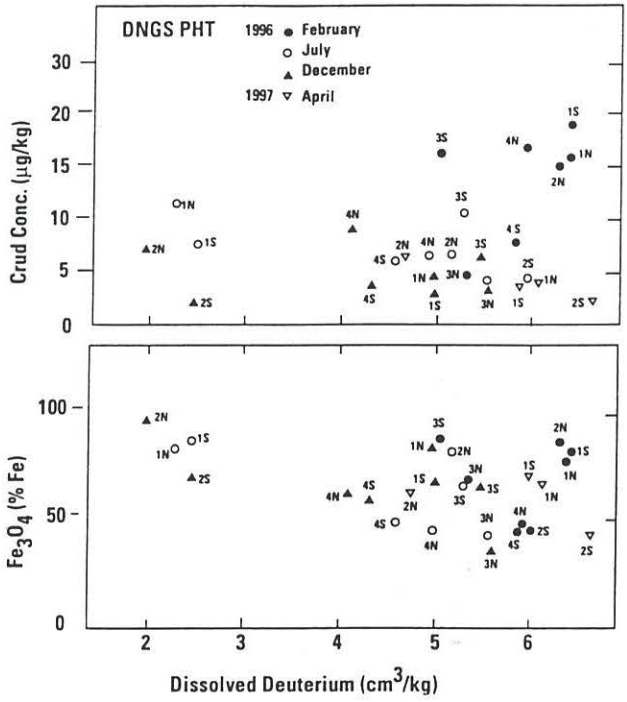

Figure 7. Crud concentrations and fractions of Fe_3O_4 as a function of dissolved deuterium. Crud mass was determined by weighing.

More systematic and accurate PHT water sampling is required to validate preliminary findings discussed in this paper. In particular, the accuracy of pH_a measurements and crud mass determination has to be improved. The presence of zirconium in crud, often up to 10 to 30 wt.%, should be measured in individual cases and subtracted from the total crud concentrations. Also, it has been observed that high variability in pH_a prior to crud sampling has usually promoted crud transport. Finally, ion-exchange filters (behind particulate filters) should also be used in addition to particulate filters to determine the solubles/crud ratio.

The mechanism for formation of crud particles in PHT system is not well understood. It is believed that iron is removed from carbon steel components by general cor-

rosion and flow-assisted corrosion (dissolution), especially in areas where water stream is unsaturated in iron, such as outlet feeders. On lay-ups the general corrosion probably increases considerably. During on-power operation, iron may reprecipitate in areas where it is oversaturated, particularly because of temperature drop, such as outlets of SG pipes. Thus, the deposits on the filters can contain particles formed in two different mechanisms: 1. the particles precipitated on system surfaces and removed (spalled) by process streams, 2. the particles precipitated from Fe dissolved in water during migration (cooling) to filter. High temperature sampling would help to distinguish between those two mechanisms.

A better understanding of iron oxides dissolution and reprecipitation processes in PHT system is also needed in the context of possible depleted zinc treatment. It was shown in reference [17] that in simulated CANDU primary coolant Fe and Zn tend to co-precipitate on carbon steel surface in the form of zinc ferrite ($ZnFe_2O_4$) particles. This process may require and consume large quantities of isotopically depleted zinc.

The relationship between oxidation state of Fe and concentration of dissolved O_2 in PHT water is yet to be established. In general, reduction-oxidation of primary-side iron can be affected by:

- external sources of oxygen; and
- oxygen from radiolysis.

External Sources of Oxygen

The main heavy-water storage tank has a cover gas, but condensate and makeup water can be air saturated (at Bruce B and DNGS it is). Fueling machines (FM) can introduce some oxygen from FM water (if it is oxygenated), because the storage tank for FM water in DNGS is open to air. Further, heavy water from valves, sampling lines, drains, etc., is usually collected in a tank (gravity system), which is open to air.

Starting from the middle of 1996, a nitrogen blanket was used during shutdowns, both in the main circuit and in the condensate and bleed tanks. Although its main purpose is to purge D_2, it also helps to keep the pH_a high, and, as it appears now, it facilitates establishing more reducing conditions (more magnetite) in the PHT system.

Figure 8 shows a comparison of ^{41}Ar in reactor inlet water in DNGS Units 1 to 4. As seen, since introduction of N_2 blanketing procedure much lower surges of ^{41}Ar (a product of airborne ^{40}Ar activation) have been observed after recent start-ups. This may be the main reason that iron in corrosion products is recently less oxidized than it has been in the past, prior to N_2 blanketing (cf. Figure 5 for comparison).

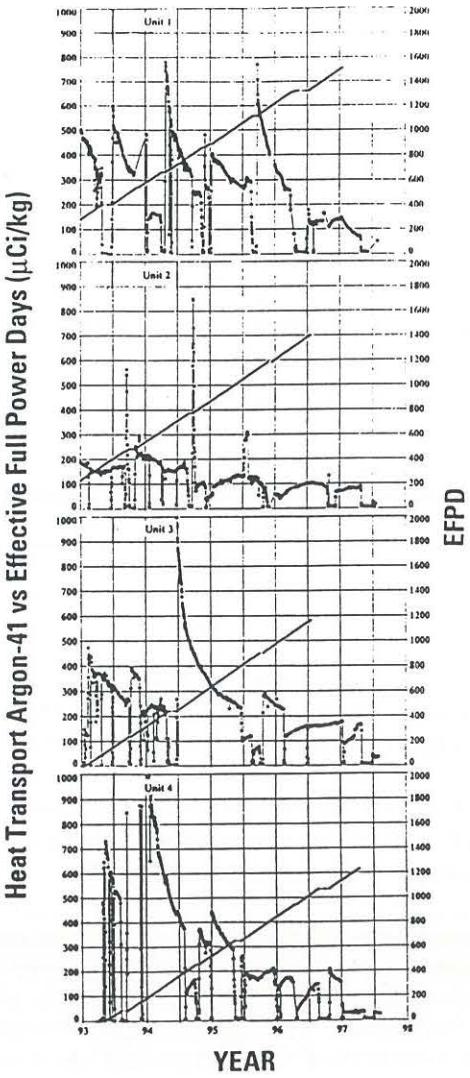

Figure 8. Activity of ^{41}Ar in reactor inlet water in DNGS Units 1 to 4, as a function of time.

Oxygen from Radiolysis

Oxygen production from radiolysis can be affected by:

- reactor power; and
- steam quality.

Steam quality is probably the most significant. At present, the outlet steam quality is probably in the following order: CANDU 6 > Darlington > Bruce-B > Bruce-A > Pickering. Reactor age may play a role in determining outlet steam quality, largely because of the tube creep.

In reactors with boiling at the outlet of the channel, deuterium is stripped into the vapor phase, leaving less deuterium to suppress radiolysis. This is probably not a case of DNGS.

To prevent radiolysis and O_2 productions, in DNGS, deuterium is added at concentration of 3 to 10 cm^3/kg D_2O. The addition is stopped 1 to 2 weeks before scheduled shutdowns and then the system is degassed.

There is little experience in crud analysis and iron speciation in other stations. A Gentilly-2 study showed 100% magnetite (in 3 specimens examined thus far) [18]. Bruce B had orange (ferric) crud when operating at 100% (with boiling); since the reactor was derated, cruds have been black (magnetite). The analysis of crud filters from Bruce B is in progress.

5. Conclusions and Recommendations

The objectives of this work were to develop procedures for monitoring the corrosion product transport in the primary side of CANDU reactors, and to gain an insight into the composition of the transported crud. Such measurements are much needed as there are few field data.

Regular sampling of primary side water and analysis of crud is important for proper maintenance of CANDU reactors. The expected goals and benefits include:

- identification of the origin of oxidized iron and zirconium species;
- recommendations on how to lower crud and activity transport;
- help in minimizing FAC effects and feeder degradation to maxime lifetime and performance of the system; and
- help in minimizing occupational dose and radioactive waste.

From our work performed until now on CPT monitoring of the PHT one can arrive at following specific recommendations and control actions:

- During lay-ups and shutdowns, air in-leakages may cause considerable corrosion of carbon steel components, reflected in start-up crud bursts up to ~10 ppm. Nitrogen blanketing is a good remedial action.
- Because iron transport in steady-state is correlated with pH_a, and may reflect increased FAC rates, the use of pH_a lower than 10.3 to 10.4 should be considered, if steady-state iron levels continue to be above 5 ppb.of total Fe, remedial measures to ensure more reducing conditions should be considered.
- Periodic monitoring of the oxidation state of corrosion products at steady-state is highly recommended. If magnetite levels are below 80% of total Fe, remedial measures to ensure more reducing conditions should be considered.
- Presence of iron oxyhydroxides in the crud indicates air in-leakage's and should be minimized by heavy-water system leak-proofing and nitrogen blanketing.
- Concentration of Zr in the crud higher than ~1 ppb may indicate excessive wear of fuel bundle pads and pressure tubes, and should be avoided.

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