CORROSION-PRODUCT TRANSPORT, OXIDATION STATE AND REMEDIAL MEASURES

Jerzy A. Sawicki, Michael E. Brett* and Robert L. Tapping

ABSTRACT

The issues associated with monitoring and controlling corrosion-product transport (CPT) in the balance-of-plant (BOP) and steam generators (SG) of CANDU stations are briefly reviewed. The efforts are focused on minimizing corrosion of carbon steel, which is used extensively in the CANDU primary and secondary systems. Emphasis is placed on the corrosion-product oxidation state as a monitor of water chemistry effectiveness, and as a monitor of system corrosion effects. The discussion is based mostly on the results and observations from Ontario Hydro plants, and their comparisons with PWRs. The effects of low oxygen and elevated hydrazine chemistry are reviewed, as well as the effects of lay-up and various start-up conditions. Progress in monitoring electrochemical potential (ECP) at Ontario Hydro plants and its relationship to the oxidation state of corrosion products is reviewed. Observations on corrosion-product transport on the primary side of steam generators are also discussed.

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1. INTRODUCTION

The principal objective of the steam generator (SG) owner–operator is to keep the SG in service as long as possible with as little maintenance as possible. The SG is the ultimate repository of any poorly chosen chemistry or of any breakdown in water chemistry, and the consequences can be corrosion or fouling or both. Corrosion-product particulates originate from various sites in the primary and secondary system of nuclear reactors and are transported and deposited in the SGs. These particulates can cause a variety of problems, such as decrease of heat-transfer capability through deposition on tubes, a limitation of flow in some restricted areas (for instance, tube-to-tube support plate crevices), and an acceleration of corrosion in crevices, either in deep sludge piles or at blocked tube supports. The influx of oxidized corrosion products may have a particularly adverse effect on the redox environment of SG tubing, thereby increasing the probability of localized corrosion, such as pitting, intergranular attack and intergranular stress-corrosion cracking.

Operationally, fouling and corrosion are controlled by the rigorous application of appropriate chemistry specifications. Ideally, water chemistry should be based on electrochemical potential (ECP) data, but this information is as yet virtually unavailable. However, the iron oxidation state can provide clues to the effectiveness of feedwater (FW) chemistry control strategies in maintaining reducing conditions in the secondary cycle. A reducing bulk water SG chemistry for a mixed feedtrain should result in copper metal and cuprous oxide being found in the SG, along with magnetite.

It is apparent that not only the quantity of corrosion products but also their redox nature may influence corrosion processes in the steam SGs. In particular, control of the oxidation state of iron-based corrosion products, for example, Fe^{2+} vs. Fe^{3+} species may minimize the risk of SG corrosion if the transport of reducible oxides is limited, e.g., by use of elevated hydrazine concentrations. One way to reduce susceptibility to intergranular attack may be to minimize the introduction of oxidizing agents such as ferric (Fe^{3+}) oxides, especially α-Fe_2O_3, α-FeOOH and γ-FeOOH. At reducing conditions, these species are partly reduced to magnetite in FW environments. Also, the removal of copper-bearing alloy condenser and FW tubes allows not only total corrosion-product transport (CPT) reduction by allowing higher pH operation in the balance-of-plant (BOP), but this removal also eliminates the transport of oxidized Cu^{2+} species.

Systematic surveys of the corrosion-product species transported in Ontario Hydro CANDU reactors started in 1990. The results of secondary-side surveys were earlier reviewed in References 1 to 4., and a detailed summary of primary-side study is given in Reference 5. The surveys helped to mediate corrosion and transport of oxidized particulate corrosion products, by design changes and by improvements in operational procedures.

Regular FW corrosion-product monitoring is also important for performance indicator reporting, such as the OHN Steam Generator and Reactor Chemistry Index (SGRCI) and the World Association of Nuclear Operators (WANO) index for pressurized-heavy-water reactors.

2. CORROSION PRODUCTS

The corrosion products are analyzed using X-ray fluorescence (XRF), X-ray diffraction (XRD), and Mössbauer spectroscopy. Details of these analytical procedures are discussed in Reference 6. Table 1 lists the corrosion-product species identified in CANDU primary and secondary water systems.

Table 1: Corrosion-Product Species Identified in CANDU Reactors.
ROH = reactor outlet header, CEP = condensate extraction pump, FW = feedwater, BLD = boiler blowdown

Chemical Formula	Mineral Name	Oxidation State	ROH	CEP	FW	BLD	SG Sludge
α-Fe	metallic iron	Fe(0)	-	minor	minor	minor	-
Fe_3O_4	magnetite	Fe(II),2Fe(III)	major	major	major	major	major
$Fe_{1-x}O$	wüstite	Fe(II)	-	minor	-	-	-
α-FeOOH	goethite	Fe(III)	minor	major	major	-	-
γ-FeOOH	lepidocrocite	Fe(III)	minor	major	major	minor	-
α-Fe_2O_3	hematite	2Fe(III)	major	major	major	major	minor
γ-Fe_2O_3	maghemite	2Fe(III)	-	minor	-	-	-
$NiFe_2O_4$	trevorite	Ni(II),2Fe(III)	-	-	-	-	major
$ZnFe_2O_4$	franklinite	Zn(II),2Fe(III)	-	-	-	major	major
$CuFe_2O_4$	copper ferrite	Cu(II),2Fe(III)	-	-	-	minor	major
Cu	metallic copper	Cu(0)	-	-	minor	minor	major
Cu_2O	cuprite	2Cu(I)	-	-	minor	minor	minor
CuO	tenorite	Cu(II)	-	-	minor	minor	minor
β-$Zn(OH)_2$	zinc hydroxide	Zn(II)	-	-	-	minor	-
Zn_2SiO_4	willemite	2Zn(II)	-	-	-	minor	minor
ZrO_2	baddeleite	Zr(IV)	minor	-	-	-	-

The insoluble corrosion products are largely iron oxides and oxyhydroxides in all-ferrous feedtrains and a mixture of iron and copper oxides in mixed feedtrains. The presence of metallic iron is sporadic and is ascribed to the physical erosion of carbon steel components, especially in fast wet steam flows. The reduced iron oxides are predominantly magnetite (Fe_3O_4), and wüstite ($Fe_{1-x}O$), which is rarely observed. The reducible iron oxides and oxyhydroxides observed are predominantly hematite (α-Fe_2O_3), goethite (α-FeOOH) and lepidocrocite (γ-FeOOH). Mixed oxides (spinels) are common in mixed feedtrain units; for instance, nickel ferrite ($NiFe_2O_4$) is found in the Pickering Nuclear Generating Station (PNGS) SGs. The presence of $NiFe_2O_4$ in boiler deposits has been linked to oxidizing conditions in the low-temperature region of the feedtrain, which can result in the transport of Cu(II) species to the SGs. Cu(II) is a strong enough oxidizing agent to oxidize NiO and Fe_3O_4 to $NiFe_2O_4$, whereas Cu(I) is not [7]. Zinc is often found with copper because many of the copper alloys are brasses, and zinc oxides and ferrites may be present. Although oxide films form on SG tube surfaces, these alloys generally do not corrode sufficiently that the oxides become a significant contributor to the SG oxide corrosion-product inventory.

3. SECONDARY-SIDE SURVEY

On the secondary side, iron oxide sludge is mostly generated by corrosion of carbon steel piping surfaces—especially in regions of lower pH, such as the wet steam downstream of the high-pressure turbine—and in the condenser. Flow-assisted corrosion (FAC) may be a significant contributor to CPT, especially in areas where water is unsaturated in iron, for instance, in wet steam lines, lines where flashing can occur, components that are exposed to significant turbulence (valves, etc.) and areas where significant flow and temperature changes occur (reducers, elbows, tees).

All sources of CPT are a concern because the deposition of corrosion products in the SG can lead to various undesirable phenomena:

- reduced heat transfer (i.e., increasing reactor inlet header temperature, RIHT). However, Ontario Hydro's experience with the removal of copper-containing secondary-side tube deposits at PNGSs A and B and at Bruce Nuclear Generating Station A (BNGS A) indicated that this removal has not produced any improvement in RIHT.

- increased impurity hideout in fouled areas such as the tube-sheet sludge, i.e., end-tube support plates and even tube free-span surface deposits, which can lead to localized corrosion.

- thermohydraulic instability because of significant blockage of upper bundle tube support plates (as observed at BNGS A). Transport of copper and zinc to SGs may also cause considerable hardening of the deposited sludge. In addition, fouling in the balance-of-plants has reduced the efficiency of secondary system components such as flow venturis in US pressurized-water reactors (PWRs).

Generally, it is understood that SG tubing is susceptible to secondary-side corrosion under oxidizing conditions (hence the drive to maintain reducing conditions and to limit total oxidant ingress), and is susceptible to corrosion under deposits and in crevices (hence the drive to minimize the total fouling burden to the SG and also impurity ingress). Deposits exacerbate all types of localized corrosion by making existing crevices and junctions between supports and tube walls less open and more able to concentrate ionic impurities to aggressive levels. Corrosive impurities include oxygen, ferric and cupric ions, chloride, reduced sulphur species (sulphides, thiosulphates), and acid sulphates.

To suppress the formation and transport of corrosion products to the SGs and to maintain minimum corrosion potential in the boiler FW, an all-volatile chemistry is used with hydrazine

(N_2H_4) treatment of the FW. Ontario Hydro CANDU stations operate at >100 ppb FW hydrazine. Hydrazine is a strong reducing agent at FW and boiler temperatures, especially in the pH range 9 to 10.5. Typically, in CANDU reactors, hydrazine is added between the deaerator (DA) and the DA storage tank, to control FW oxygen. The thermal decomposition of hydrazine generates ammonia, which helps sustain a high pH. For carbon steel protection (as well as SG tube protection) the pH (25°C) is maintained at 9.5 or greater for an all-ferrous BOP, or in the pH range 8.8 to 9.3 (or sometimes higher) for a mixed copper–ferrous BOP. High pH reduces FAC also, but FAC is more likely to occur under reducing conditions (dissolved O_2 less than some critical value, probably <5 ppb, but probably temperature-dependent) than under oxidizing conditions. Hence the SG and BOP requirements for oxygen may be different and conflicting, depending on the degree of, or concern about, FAC in the secondary piping. There are several other similar conflicts for mixed ferrous–copper systems. For instance, increased oxygen in-leakage requires increased use of hydrazine to maintain reducing conditions in the SG. Residual hydrazine in the SG decomposes to produce ammonia, which, in the presence of oxygen, can lead to increased corrosion of copper-bearing alloys in the condenser and low-pressure (LP) heaters.

Steady-state CPT

Corrosion products are sampled regularly (weekly at OHN plants) from unit FW and are analyzed to provide an assessment of secondary water chemistry and, less frequently, they are sampled from condensate extraction pump (CEP) and at boiler blowdown (BLD), to provide an assessment of condensate and SG chemistry. This sampling enables a direct assessment of total CPT burden to the SGs, which provides the fouling rate and an indirect assessment of SG bulk and crevice chemistry, and hence secondary and SG water corrosivity to tubes, shell, support structures and other SG internals.

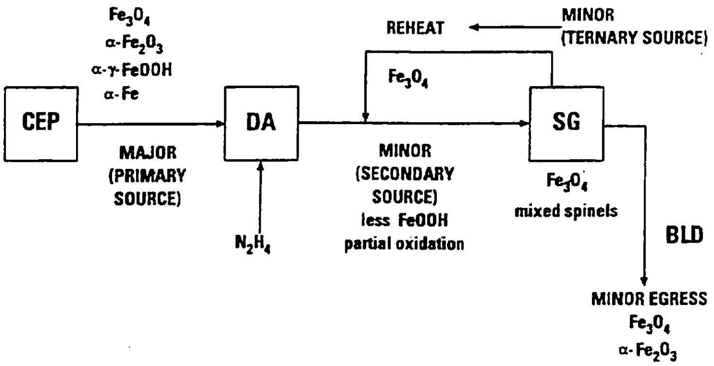

Figure 1: Main sources and chemical form of iron crud in the secondary water system of CANDU reactors. CEP is the condensate extraction pump, DA is the deaerator, SG is the steam generator, and BLD is the blowdown.

The major iron oxide sources and phases are shown in Figure 1. The figure shows that condensers are a major source of corrosion products and that the corrosion products there and in the FW are highly oxidized. The principal sources of oxygen are from poor air-extraction, air in-leakage, oxygenated makeup and other oxygen-rich streams, such as the gland seal waterrecovery tank, which feeds back into the condenser. The relative significance of the sources can vary considerably with condenser design, especially inlet locations (e.g., above or below the water line) for feedback streams.

Boiler blowdown as a means of iron crud removal generally appears to be quite inefficient. Ontario Hydro's plant estimates of removal of iron crud have ranged from 5% to 25%. Blowdown sampling typically shows a higher percentage of magnetite (although usually not 100% for CANDU plants) than does FW sampling, which indicates that the SG chemistry is indeed more reducing than elsewhere in the FW system. This trend is consistent with general PWR experience [8]. It is interesting to note that Gentilly-2 (Hydro-Québec) does not add hydrazine and has significantly more oxidized blowdown corrosion products (only 45% to 50% Fe as magnetite) than the Ontario Hydro units have.

The percentage of magnetite is a strong function of sampling location. As Figure 2 shows, corrosion products in CANDU FW are more oxidized than those in the condensate in contrast to corrosion products in FW of Japanese and US PWR units, where it becomes more reducing than in the condensate. This oxidation of corrosion products occurs even though CANDU systems employ a DA and inject hydrazine between the DA and the DA storage tank, which is something that the PWRs stations generally do not do.

The kinetics of iron oxide reduction by hydrazine are relatively slow (about 4 h to convert lepidocrocite of various morphologies to 100% magnetite at 150°C [9]]), especially relative to the secondary-system cycle time. Also, iron oxides remaining in the SG are likely more reduced than those produced by BLD sampling (the latter may also be precipitated from solution as a result of sample cooling). This observation is consistent with phase analysis of deposits from SG deck plates, cyclone separators, U-bends, and tube sheets, which often indicate a lower hematite fraction than BLD filters do.

The corrosion products in PWR FW are likely more reduced than in the condensate because of the relatively large contribution of corrosion products from high-temperature drains, which contribute approximately 30% to the total FW flow, and add ~8 to 10 ppb Fe, mostly in a form of magnetite. These drains are a relatively minor source of corrosion products for CANDU reactors, where high-temperature drains contribute ~15% of total FW flow, at Fe concentrations not very much above those in the main stream. In CANDU plants, the DA serves to provide a residence time of several minutes for the FW in the circuit. The residence time for particulate species may be even longer, during which time the corrosion products will tend towards thermodynamic equilibrium. Under these conditions, even 5 ppb dissolved oxygen produces hematite as the thermodynamically stable product [10]. It is probable that the corrosion products sampled from the FW after the DA storage tank are a mixture of partially oxidized species that have passed through after a somewhat extended residence time and completely oxidized material re-entrained from the vessel's internal surfaces. Thus a net conversion from magnetite to hematite is observed across the DA and DA storage tank in CANDU plants.

Although the pH requirements for the SG and BOP are generally mutually consistent, this is not necessarily the case for the dissolved oxygen requirements. Low oxygen (<5 ppb) is required in the SG to protect the tubes, and FAC of carbon steel components in the SG is not expected to be a concern under normal all-volatile treatment (AVT) conditions (although thinning of support plate ligaments at Gravelines, Electricité de France, has been attributed [11] to FAC in units operating with an ammonia-only chemistry). However, in the BOP, especially areas susceptible to FAC, higher oxygen concentrations

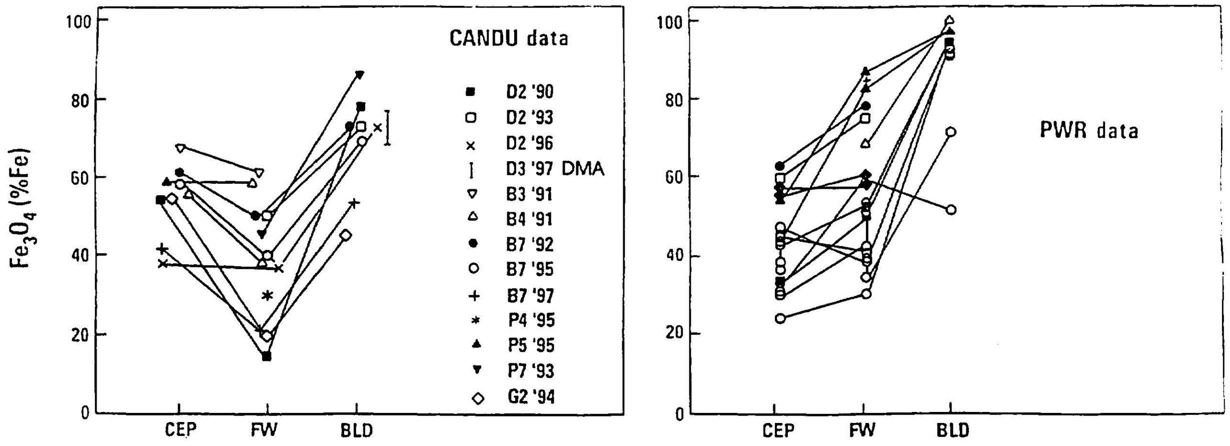

Figure 2: Fractions of Fe_3O_4 in CEP, FW and BLD in PWR and CANDU secondary-side, based on Mössbauer analyses at CRL.

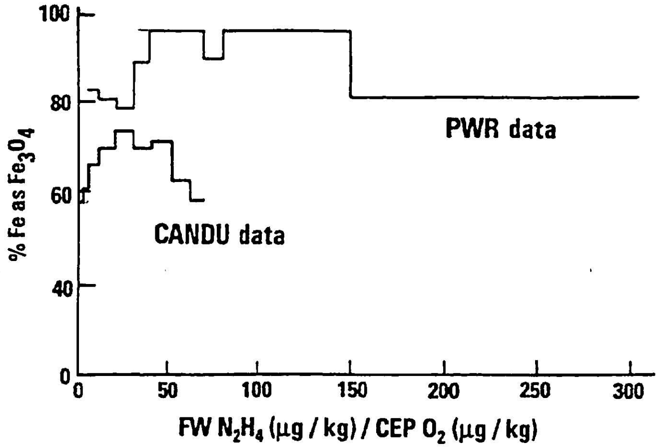

Figure 3: Fraction of BLD Fe_3O_4 as a function of FW hydrazine-to-CEP oxygen ratio based on many averaged data from OHN CANDU stations and PWRs.

(>5 ppb) may be required to maintain the protective oxide surface. Although high oxygen concentrations in the BOP likely result in more highly oxidized iron-based corrosion products, the issue of whether this results in a net increase in the ingress of oxidant to the SGs is currently under investigation.

High (≥100 ppb), or even very high (>200 ppb), hydrazine chemistry control is practised by a number of PWRs. A minimum value for FW hydrazine for all-ferrous systems is either ≥8 times condensate oxygen concentration or >20 ppb, whichever is greater, as specified in recent EPRI guidelines (Revision 4) [12]. However, it is stressed that in PWRs, hydrazine should be maximized, with a possible range of 100 to 500 ppb in FW to maintain >95% magnetite in the SG BLD corrosion products.

The rationale for this is based on the data shown in Figure 3, where the percentage of magnetite in the SG blowdown is plotted as a function of the ratio FW N_2H_4/CEP O_2. CANDU data are based on over 90 measurements—and PWR data on over 30 individual measurements—performed at CRL up to 1998 April. In general, the data indicate that increasing values of the ratio favour magnetite formation, which implies a reducing chemistry in the SG.

For CANDU stations, increasing the ratio did lead to an increase in Fe_3O_4 up to a ratio of ~30, but all further increases in the ratio have shown a decrease in the Fe_3O_4. However, there are very few CANDU data for ratios higher than 30, and these were achieved for short time periods at high N_2H_4 concentrations. It appears to be difficult to produce >80% magnetite in a CANDU SG blowdown. This trend may be a consequence of a number of factors related to the kinetics of oxide conversion, such as lower SG operating temperatures for CANDU plants (lower by ~20°C to 25°C than in PWRs) and BOP design differences giving rise to different particle residence times, in particular, the greater opportunity for hematite production in the DA.

BOP Survey

A survey of general corrosion deposits performed in BNGS B, Units 5 to 8, helped to identify the origin, evolution and inventory of corrosion products along the secondary system of CANDU reactors [2]. Various locations along the secondary system were inspected, and about 80 specimens were taken by scraping or abrasion. The data from Unit 8 were especially valuable because they represent the status of the secondary system after operating for ~700 consecutive days. The sample locations of special interest were (1) the sides of the condensers above and below the water line, on areas of fresh corrosion; (2) suction piping and discharge piping between the condensate pump and first heater; (3) the low-pressure heater tube side; (4) the side of the DA storage tank, relief valve line, and feed-pump recirculation line; (5) the boiler feed-pump discharge before the high-pressure heater; (6) areas between the high-pressure heater and the preheater; (7) the shutdown cooling loop between the preheater and boiler; (8) the high-pressure heater shell-side drains between the drains pump and the DA; (9) the steam discharge to the condenser; and (10) the high-pressure turbine exhaust line before the moisture separators.

A variety of corrosion products were identified including magnetite, hematite, maghemite, goethite, lepidocrocite and wüstite. Very high percentages of magnetite were observed on components exposed to steam, whereas large amounts of hematite were found in the DAs and on associated piping. Maghemite was found only in areas exposed to temperatures below 30°C to 40°C. Low-temperature phases, such as goethite and lepidocrocite, were largely absent from components exposed to temperatures higher than 100°C to 150°C (i.e., in FW and SGs).

Several trends were apparent. Deposits from high-temperature drains or areas generally associated with steam were almost 100% magnetite, which corresponded well with results from filtered corrosion products. This finding is reasonable because corrosion products from other parts of the secondary system (such as the condensate) are not carried over into these streams, and hence the internal pipe surfaces in these regions are the only source for the release of corrosion products. In the main feedtrain, corrosion products may be formed in one location and swept forward before being sampled, and hence may not reflect local conditions at the sampling location. Deposits from the DA storage tank and in valves downstream of this vessel contained hematite in proportions ranging from 80% to 100%. The contribution to the filtered FW deposits from these sources of hematite may account for the fact that FW corrosion products are more oxidized than those sampled at the CEP in CANDU plants.

Startups

Considerable corrosion-product generation can occur during unit shutdowns or layups. This situation is a consequence of air ingress, and it may be a major factor in transient crud bursts. Thus measures need to be taken to minimize air ingress, especially on wet components, or to reduce humidity below 35% in vessels and piping drained and open to air. Plant measurements to isolate the major factors affecting startup and crud bursts are needed. High γ-FeOOH levels observed during unit startup suggest that active corrosion is occurring at this stage.

The transients, such as unit startups, unit trips or rapid power reductions, as well as valving out a bank of FW heaters, generate large corrosion-product bursts, relative to stable at-power operation. The contribution of startup to the total sludge burden and oxidation state is variable. Because startup crud bursts generate 100 to 200 times larger corrosion-product concentrations than steady-state operation does, it is estimated that 50% or more of the total CPT could arise from transients. In addition, startup can inject considerably larger fractions of oxidized species and, especially, γ-FeOOH. Field data suggest that during startup, γ-FeOOH transported from the condensate does not have sufficient time to decompose to any great extent before entering the SG. Figure 4 compares 2 different BNGS B startups with associated transients in dissolved condensate oxygen, FW hydrazine, and FW iron oxides concentrations. It is evident that in startup with initially low and slowly increasing hydrazine dosing, there was a prolonged transport of γ-FeOOH and that the reducing conditions in FW were only achieved in 5 days. More data about startup crud bursts are presented in Reference 6.

A better understanding of startup crud bursts and the overall significance of the ingress of more highly oxidized iron species is imperative in the context of hydrazine optimization to minimize environmental emissions. Efforts to chemically reduce the iron oxides (e.g., by excess hydrazine dosing consistent with environmental discharge limits (currently 50 mg/kg for OHN), especially during the period when the secondary system is hot but flow is low, thereby generally increasing the time available for reaction) and to physically remove loose crud generated during shutdown and layup are expected to be beneficial.

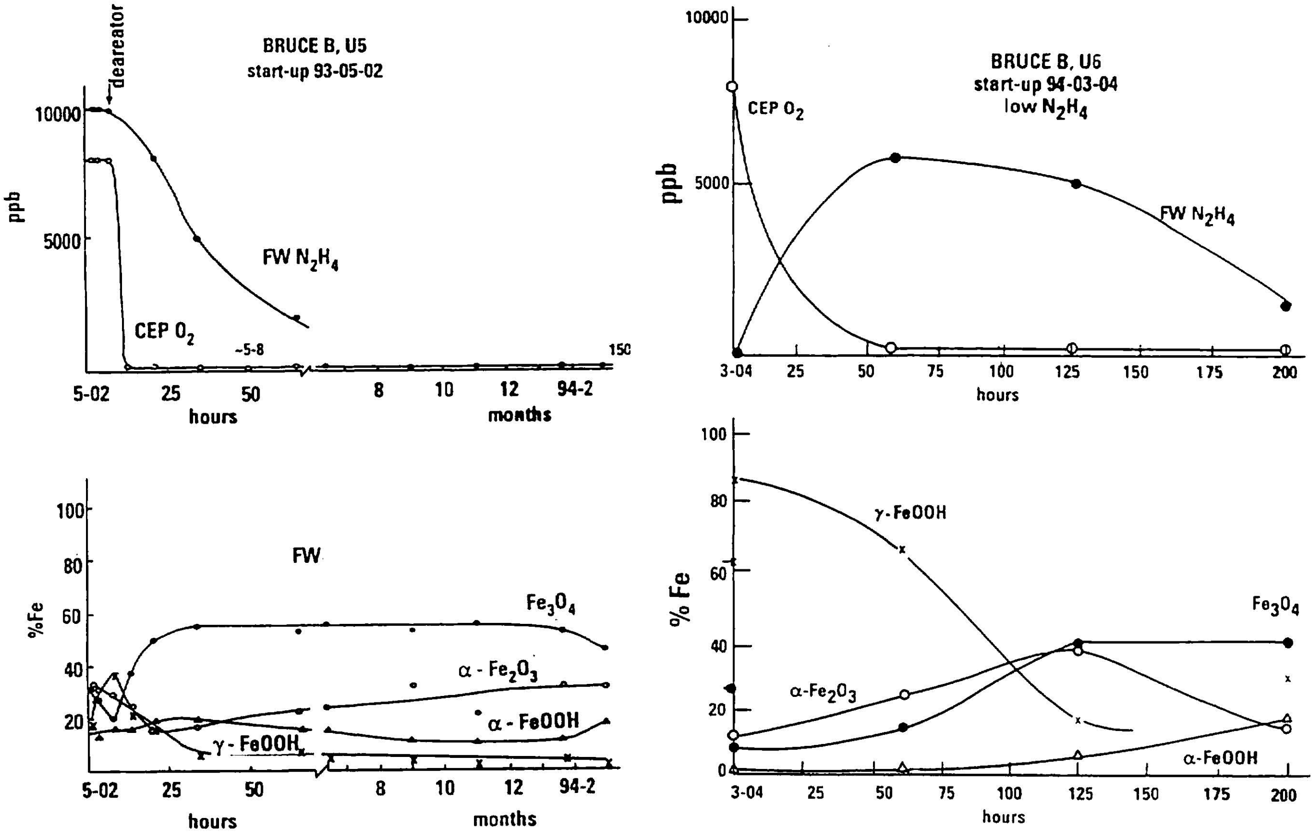

Figure 4: Crud transport during startups of BNGS B Units 5 and 6 at drastically different hydrazine dosing modes.

The ECP Program

Corrosion is an electrochemical process, and the driving force for it is based on redox potentials, established between the component material and the environment. Electrochemical potential is an important parameter in assessing the susceptibility of SG tubing to corrosion, and it is expected that maintaining a reducing condition in the SG bulk water will provide an ECP in the correct range in the crevice to minimize corrosion of SG tubes. It is not yet known what the values of the potential are in the susceptible areas of the SG (i.e., in crevices), or whether the chemistry required to obtain this ECP range will also produce a minimum CPT rate. The ECP tests at OHN (BNGS B, Unit 7; PNGS A, Unit 4; and BNGS A, Unit 4) and correlations between ECP and the redox state of corrosion products are described in Reference 3. The typical values of steady-state ECP measured vs. standard hydrogen electrode (SHE) are listed in Table 2.

Table 2: Electrochemical Potential in Ontario Hydro CANDU Plants

Sampling Site	Electrode Potential (mV vs. SHE)			
	Pt	I600	M400	Carbon Steel
BNGS B, Unit 7 Feedwater	-510 to -530	-590 to -600	--	-560 to -580
PNGS A, Unit 4 Feedwater	-470 to -490	--	-480 to -500	-630 to -640
BNGS A, Unit 4 Condensate	-60 to -70	-100 to -110	--	-260 to -270

Recent measurements at several CANDU stations show that hydrazine additions have little effect on the secondary-system oxide-phase composition. These measurements were correlated with ECP measurements [3], which were also found to be less sensitive to oxygen and hydrazine concentration changes than were ECP measurements in PWRs. This difference can possibly be ascribed to the use of DAs in CANDU systems. This finding is contrary to recent laboratory experiments, where a strong relationship between magnetite fraction and ECP was observed at FW conditions [13]. In these experiments, the effect of oxygen and hydrazine changes was more visible on Pt and Alloy 600 electrodes than on a carbon steel electrode.

4. PRIMARY-SIDE SURVEY

The two major primary-side chemistry control requirements of CANDU reactors are the maintenance of low concentrations of dissolved oxygen (DO_2 = 3 - 10 cc/kg) to ensure low rates of zirconium alloy and carbon steel corrosion, and appropriate alkalinity (pH_a = 10.3 - 10.7) to ensure acceptable low rates of carbon steel corrosion.

Primary-side CANDU SG thermal degradation manifests itself mainly by a rising reactor inlet header temperature (RIHT). It is ascribed primarily to fouling of the primary side of the SG tubes and leakage from divider plates. Primary-side fouling effects are related to thermal resistance associated with deposits and increased hydraulic resistance caused by decreased SG tube volume.

A systematic survey of primary-side CPT is being performed at Darlington NGS Units 1 to 4 [5]. The D_2O from reactor outlet headers is cooled to 50°C and sampled using 0.45-μm membrane filters The deposits contain Fe, mostly from carbon steel corrosion, and some Zr (~5 to 20 wt % Fe), from the wear of Zircaloy fuel bundle pads and Zr2.5Nb pressure tube fretting.

In the beginning of the survey in 1994 and 1995, the crud bursts were as high as 8 mg/kg D_2O and contained up to 70% to 80% Fe in the form of oxidized iron species (hematite, lepidocrocite, goethite and ferrihydrite). The steady-state crud concentrations were then often as high as 20 to 30 μg/kg D_2O, with only 40% to 60% Fe in a form of magnetite. In recent steady-state runs, as a result of better oxygen control during layups (nitrogen blanketing) and better pH control (lower and more stable values), the crud transport was lowered to 3 to 5 μg/kg D_2O, mostly as magnetite (60% to 80% Fe) and hematite (20% to 40% Fe).

It was found that the crud concentration increases markedly with pH_a in the range $pH_a = 10.3$ to 10.7 [5]. This value agrees with the trend predicted by flow-assisted solubility of magnetite in lithiated water at ~300°C, and it is generally in accord with the model of dissolution, transport, and redeposition of iron in the primary-heat-transport system of CANDU reactors [14]. Operation at the lower end of the pH_a range has recently been recommended to the OHN stations [15].

5. RECOMMENDATIONS

Not only the quantity, but also the redox state, of corrosion products transported to the SGs can have an effect on their long-term performance. A number of design and operational options exist to minimize the transport of corrosion products and other oxidizing species to the SGs during the different unit operating states. The design options are not discussed here, but some operating recommendations are presented:

- Maintain iron levels in FW during steady-state conditions at less than or equal to 2 ppb, in agreement with current Ontario Hydro practice.
- Compare predictions of total SG sludge loading obtained from CPT data with the results of in-service inspections, such as visual, eddy current or ultrasonic inspections or tube removals. Obtain sludge from well-defined areas of the SG, where possible, for phase characterization.
- Operate with a sufficient hydrazine-to-oxygen ratio so that the blowdown sludge is predominantly (>75%) magnetite.
- Perform routine CPT monitoring of FW. Consider the use of alternate amines, such as ETA, if CPT iron levels remain higher than specified. The major sources of corrosion products and the areas where pH_t is maximized are critical to the evaluation of various pH control options.
- Perform periodic monitoring of the oxidation states of corrosion products, especially in SG blowdown. The trends are useful to establish the optimum level of hydrazine. To determine the magnetite fraction, Mössbauer spectroscopy is the method of choice.
- In preparation for unit startup, minimize the time spent before startup with the secondary system hot but with high oxygen. Where discharge restrictions and secondary-system materials allow, dose with a large excess of hydrazine to lower dissolved oxygen, reduce oxidized iron oxides, and hence minimize the total oxidant transport to the SGs.

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DISCUSSION

Authors: J.A. Sawicki, M.E. Brett, R.L. Tapping, AECL and Ontario Hydro Nuclear

Paper: Corrosion-Product Transport, Oxidation State and Remedial Measures

Questioner: J. Gorman

Question/Comment:

How important do you think oxidizing conditions at the top of tubesheet caused by ingress of oxidizing corrosion products (hematite and copper oxide) are to the occurrence of IGA/SCC at that location?

Response:

It is difficult to comment on the relative significance of one contributing factor to top of tubesheet IGA/SCC versus the others. The presence of oxidizing species will tend to raise the ECP. Copper species appear to raise potential more than the reducible iron oxides such as hematite. Also, soluble oxidized copper species are more likely than insoluble species to be able to migrate to areas of concern, such as top of tubesheet when a sludge pile is present. It is less clear how relatively insoluble species such as hematite would contribute to the ECP locally in this case. Nevertheless, the influx of oxidants to the steam generators generally appears likely to be a contributing factor to IGA/SCC. In the specific case of Bruce-A, it seems highly likely that oxidant ingress, including oxygen, has played a major role in the degradation observed at that station.

Questioner:

Question/Comment:

Is the major source of corrosion products the condenser in all the cases you have looked at, including all-ferrous feedtrain with high pH?

Response:

All of our studies at OHN have shown the condensate as the largest single contributor, even when copper does not contribute. Low temperature drains will contribute somewhat to the amount measured at the CEP discharge. However, they are difficult to sample individually. Our studies indicate that the concentrations of species in the high temperature drains may be higher than in the main circuit, but that the drains flow rate is such that the total mass transport contribution is small. It seems reasonable to suggest that the low temperature drains contribution is also small by implication. In addition, Ken Burrill has performed some work using carbon steel from the condensers removed from Pickering-B to look at the contribution of corrosion of condenser internals to condensate CPT. The condenser has a large carbon steel surface area. Ken's estimated transport numbers from corrosion of the condenser material alone are consistent with the values measured at the CEPD during our CPT surveys at Pickering. This work has been published as COG report COG-96-516.

Questioner: L. Green, AECL

Question/Comment:

Major source of corrosion products (reported to be lower temp part of feedtrain)

- for low pH, mixed feedtrain or for high pH, all-ferrous?
- what is the fraction contributed by the various drains?

Response:

Statement refers to high pH, all-ferrous system. Condensers are the major source, with drains contributing a significant, but minor fraction.

Questioner: P. Millett

Question/Comment:

Do you feel that the magnetite is being oxidized to hematite in the deaerators? Is this thermodynamically favourable?

Response:

The exact mechanism to explain the appearance of hematite at the deaerator storage tank is difficult to pin down. It may be that under the pH/redox conditions, hematite is thermodynamically stable. Hematite may also have precipitated from solution. In general, it appears that in the secondary circuit, at least up until our high-pressure heater outlets (approximately 160°C) under our typical conditions, it is more easy to oxidize corrosion products than to reduce them.