

Nondestructive Elemental Analysis of Corrosion and Wear Products from Primary and Secondary CANDU Water Circuits

Barbara D. Sawicka

*AECL, Chalk River Laboratories
Chalk River, Ontario K0J 1J0*

Abstract

The application of X-ray fluorescence (XRF) for off-line and on-line analysis of corrosion-product transport (CPT) specimens is being evaluated, to monitor corrosion and wear products in CANDU water circuits. The method is suitable for nondestructive analysis of CPT filters from both primary and secondary sides (i.e., radioactive and nonradioactive specimens). The XRF method, the portable analyzer, and the work required to optimize their performance for CPT specimens are described. Measurements performed on station CPT specimens are discussed. Data on crud transport and composition were obtained, in particular iron and lead transport in secondary-side water and iron and zirconium in primary-side water. The possibility and requirements for quasi on-line analysis under operating conditions are also considered.

1. Introduction and background information

Corrosion and corrosion-product transport in both the primary and the secondary sides of CANDU stations are important topics because of their role in the following areas: corrosion of feeder pipes, fouling of steam generators (SGs), limits on reactor-inlet header temperature, frequency of cleaning, radioactive waste, and maintenance costs. Analysis of corrosion-product transport (CPT) specimens provides information that can be used by nuclear stations as an indicator of system chemistry and that can bring a better understanding of corrosion-transport phenomena and the problems associated with these phenomena [1, 2].

Stations conduct on-line sampling of CPT by collecting specimens on filters in specially installed samplers. After the filters have been removed from the samplers, the deposits can be analyzed (off-line) using various techniques. Depending on the type of a filter used, particulate or ion-exchange, the specimen contains either suspended solids (particulate or "crud") or soluble species, obtained from circulating water streams. In some stations, secondary-side CPT specimens are routinely collected and analyzed. Primary-side specimens are usually not collected or only sporadically collected; since 1996, primary-side specimens have been collected regularly in DNGS, at approximately 3-month intervals [2].

One basic method of evaluating CPT specimens is elemental analysis, which determines the presence of

various elements and measures their content. The data, normalized to the volume of water that flows through the filters, provide the concentration of various elements in water circulating in the reactor piping (in mg or μg of the element per kg of water, i.e., ppm or ppb). The elemental analysis can be, and usually is, performed using laboratory-based wet chemistry methods, which involve specimen dissolution (digestion).

In this paper, we describe development and use of nondestructive X-ray fluorescence (XRF) methods for chemical analysis of CPT specimens, i.e., a "nondestructive and dry" method. Part of this study was reported previously [3 to 5]. The XRF method offers an advantage: because the specimens are not destroyed in the process, they can be archived and/or used in further studies using other methods, such as Mössbauer spectroscopy, X-ray diffraction analysis and scanning electron microscopy [1]. XRF is faster because no digestive step is needed; it is less labour-intensive and is therefore less costly. In the case of primary-side specimens the nondestructive XRF technique provides a more practical alternative to processing low-level radioactive waste resulting from digestive chemical methods.

It is of interest to find a method that can be used to analyze very small amounts of material, because filter deposits may be very thin. Wet chemistry methods provide excellent sensitivity for many elements, but require sufficient sample material to give high accuracy (a sample size of 0.25 to 0.5 g is preferable; if the

sample weight is too low, the dilution factor is too great and error increases).

Because it is nondestructive and because it can be very sensitive, the XRF technique is also being considered for on-line or quasi-on-line analysis. The quasi on-line examination infers that the measurements will be taken every 15 to 30 minutes, so that transient effects can be recorded and assessed. With XRF, such measurements can be performed without removing the filter from the sampler, and the analytical data record is available concurrently with the CPT sample collection, while the filter sample may be retained.

2. Experimental: The XRF method, the analyzer, and their use for CPT analysis.

XRF analysis is performed by measuring X-ray spectra and identifying energy peaks characteristic of the elements present in the sample. In XRF spectroscopy, the primary X-rays or γ -rays illuminate a sample causing it to emit X-rays characteristic of the elements present in the sample, Figure 1. X-rays for a specific element are well defined, and since there are few allowed transitions, there are relatively few X-ray peaks.

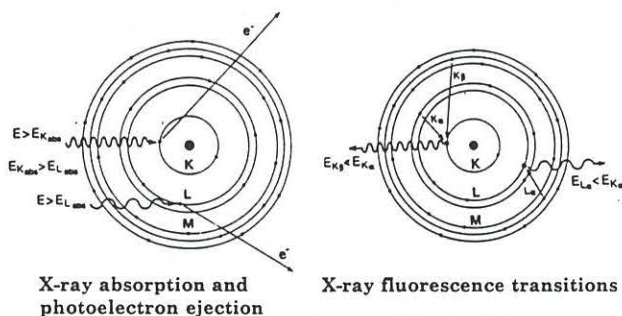


Figure 1. Principle of XRF spectroscopy.

The XRF spectroscopy analyzer can be configured in a number of different ways, but there are two basic types: wavelength dispersive XRF (WDXRF) and energy dispersive XRF (EDXRF). The distinction between the two techniques arises from the method by which the X-rays are sorted for measurements. In WDXRF, X-rays are separated according to wavelength by diffracting crystals. Such analyzers offer the best resolution, shortest analysis time and highest sensitivity, but they are element-specific and laboratory-type only.

In EDXRF analyzers, X-rays are detected by solid-state or proportional detectors and sorted electronically to produce an X-ray spectrum, which is then mathematically processed to provide the required information. These detectors allow much greater flexibility than wavelength detectors. In EDXRF, a

wide range of elements can be measured, and the elements to be measured can be easily changed, according to requirements.

The combination of improved detector resolution with advanced microprocessor technology has resulted in a new range of EDXRF analyzers, which offer new solutions to the problem of XRF analysis.

Microprocessor-controlled XRF analyzers are currently available commercially, which offer laboratory-quality analysis in portable instruments.

Quantitative analysis using XRF is based on the correlation between the amplitude of the signal and the content (concentration) of the element in a specimen. A number of factors that contribute to line intensity have to be taken into account. The details and accuracy of quantitative analysis depend on the particular analyzer hardware and software solutions; it also depends on the type of specimens, element range, geometry, line overlap, etc. The degree of line overlap is also dependent on the type of the detector.

In this work, an XMET920 [6], EDXRF analyzer, was used. Because of its sophisticated data treatment methods and high-resolution detection, this analyzer is capable of achieving much higher accuracy and sensitivity than those achieved using other portable XRF instruments. The analyzer is equipped with a Si(Li) detector, installed in a small-size probe, that is connected directly to a multichannel analyzer board (2048 channels) housed in a PC computer. The detector is cooled by a small, built-into the probe dewar of 0.5 L LN₂ capacity. The all-directional dewar enables operation of the probe in any position. The microprocessor permits instrument calibration and programming, data collection and display, and data evaluation. The detector active area is 30 mm², and the energy resolution is better than 170 eV for the K_α Mn line (5.9 keV) at 10 μ s shaping time and 1000 cps total count rate. The analyzer software automatically corrects for short-term drift (gain control) or decay of the source (autonormalization). The analyzer can be used in a portable version, suitable for field work, using an industrial-grade, portable computer (field portable XRF [6]). Using two radioactive sources, 20 mCi ¹⁰⁹Cd and 30 mCi ²⁴¹Am, the analyzer is capable of measuring elements ranging from titanium to uranium in the periodic table. The use of another source, ⁵⁵Fe, would extend the range to lighter isotopes.

The XMET920 analyzer is programmed by the manufacturer to perform some standard, although complex, functions, such as alloy analysis on bulk specimens. An important feature is that the analyzer is user-programmable. This permits us to program the analyzer for applications that require a special approach, such as high-accuracy analysis of filter deposits. The

geometry of the probe permits various detector-sample configurations.

One can perform qualitative analysis and approximate quantitative analysis of filter deposits directly from the measured spectra. The spectra show well-resolved X-ray lines for particular elements, such as iron, lead, nickel, copper, zinc, titanium, chromium, zirconium, tin and antimony. After spectra accumulation, background and peak overlap corrections are implemented, and the spectra are deconvoluted. The data needed for deconvolution calculations are obtained during instrument calibration from the spectra of single-element standards. The K- or L-series lines can be taken for analysis, depending on their energies and on what other interfering element lines might be present.

For accurate quantitative analysis of filter deposits, the analyzer has to be calibrated and programmed for a specific type of study; this is performed by developing appropriate calibration "models". The models are the instrument software and hardware configurations that are specific for a type of study, analysis range, the number of interfering elements, specimen characteristics, measurement geometry, etc. In the model, a correlation is established between the amplitude of the signal and the concentration of the element in the specimen. The models are developed by the user, by measuring a set of suitable calibration standards (i.e., known samples that are of the same type and physical form as the unknowns), and by implementing appropriate algorithms and corrections. The choice of standards, which are still being tested, is very important, and the standards should cover the range of concentrations expected in the measured specimens. Another important issue is that, for thin samples, an internal standard of a backscattered peak (which is used in the spectra deconvolution process) may vary for varying specimen thickness; tests on its accuracy and stabilization are underway.

The development of the correct calibration models for evaluation of thin filter deposits is a critical issue for quantitative XRF analysis of CPT specimens, both off-line and on-line. We made several calibration models suitable for thin-film analysis, and further tests are underway.

For XRF analysis of primary-side specimens, spectra correction for radioactive species is required and should be incorporated in the deconvolution process. The XRF measurement was integrated over a circular area of $\sim 5 \text{ cm}^2$ (diameter = 2.54 cm), which was assumed to be representative of the total CPT deposit area. Whether this is a valid assumption can be tested by repeating XRF measurements for various areas of the deposit. Smaller areas of various sizes and shapes can also be examined.

3. The specimens

A number of CPT specimens, collected during CPT surveys in Darlington NGS and Bruce B NGS, primary and secondary sides, were evaluated. These were samples of particulate corrosion products ("crud"), as no ion-exchange filters were used. $0.45 \mu\text{m}$ thick cellulose membrane filters were used. The specimens, provided by the stations, were from various sampler locations in the secondary side, including condensate extraction pump (CEP) discharge, feedwater, and blowdown water. In the primary side, the heavy water is sampled at DNGS close to the reactor outlet headers.

The deposit area was circular, about 10 cm^2 . The diameter of the deposit area varied from 34 mm to 38 mm; i.e., the area ranged from 9 to 11.5 cm^2 in various specimens.

4. Study #1: Comparison of nondestructive XRF and destructive ICP techniques for Fe analysis

To test the accuracy of XRF analysis for iron in CPT specimens, measurements were performed on a set of 19 CPT specimens, and the results were compared with the results of destructive wet chemistry analysis (inductively coupled plasma performed after specimen dissolution). The specimens were from Darlington Unit 2, taken during a CPT survey in 1996 June. Four specimens were from CEP discharge, and 15 from blowdown of boiler #1.

The XRF evaluation showed that the CEP deposits contained about 0.5 mg of iron per specimen, and the blowdown deposits between 4 and 10 mg of iron. After normalizing the XRF data to the volume of water that circulated through the filter, one obtains iron concentrations in water equal to 1 to 3 ppb ($\mu\text{g/kg}$) for CEP locations, and 15 to 40 ppb for blowdown water.

Quantitative XRF analysis was performed using calibration models developed specially for thin-film analysis. In the measurements, care was taken to monitor and stabilize the backscattered peak amplitude; the specimens were covered with an aluminium cup or aluminium plate. A number of elements other than iron were also measured in the XRF analysis, but these results will be not discussed here.

Figure 2 compares the iron concentration data obtained using the two methods of iron analysis, and shows excellent agreement between the XRF and wet chemistry data. In the evaluated range of iron contents (rather thick deposits), the XRF error that is due to statistics and calibration was ± 1 to $\pm 3\%$, and could be neglected in comparison to geometrical errors. The biggest error in the XRF evaluation of iron content is

due to the possible nonuniformity of the deposit and the variation in the deposit area (up to $\pm 10\%$). The former can be evaluated by repeating the measurements over various areas of the specimen; the latter can be eliminated by careful measurement of the deposit area. In this set of specimens, iron was found to be uniformly distributed over the filter area.

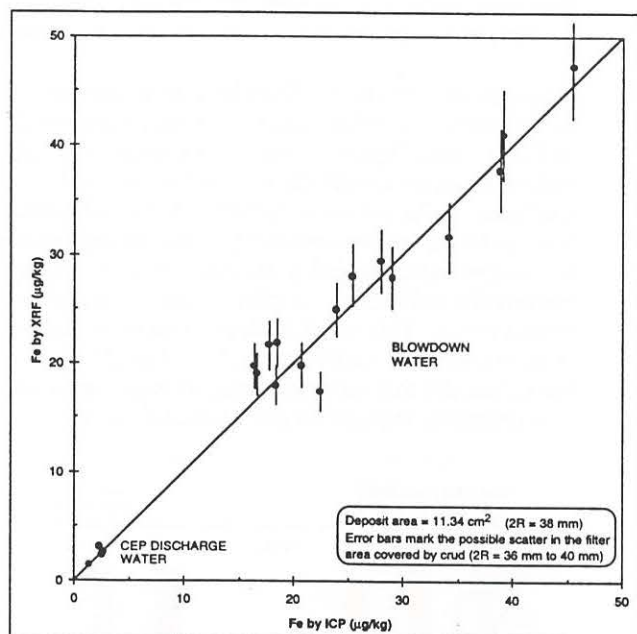


Figure 2. Comparison of XRF and ICP data on the iron concentration in water for a set of CPT specimens collected in secondary side (Darlington Unit 2, June 1996 CPT sampling). Error of XRF measurements, ± 1 to $\pm 3\%$, is increased to $\pm 10\%$ due to fluctuations in filter coverage area and specimen nonuniformity. Error of ICP measurements, not shown, is about ± 3 to $\pm 5\%$. The data are normalized to water flow and expressed in ppb ($\mu\text{g}/\text{kg H}_2\text{O}$).

The XRF error should be compared with the error of the wet chemistry evaluation. This error depends on the details of the analytical procedure, especially the control of contamination during sample dissolution and the correction for the contribution from a substrate (i.e., the "procedural blank" measurement and correction); for the range of iron measured, this error is usually between ± 3 to $\pm 5\%$, i.e., about 1 ppb. Iron content was well above the detectability thresholds of both techniques.

Good agreement between the data shows that XRF can be used instead of wet chemistry when nondestructive or quick analysis or both are needed.

Similar comparisons will be made for a larger number of specimens obtained under various station conditions, and especially for low iron concentrations (i.e., thin

deposits). For thin deposits, the geometrical error in XRF analysis will be much reduced, but the substrate contribution and detectability threshold will have to be considered. At the same time, for deposits thinner than ~ 0.25 mg, the error of the wet chemistry method might increase because of the small quantity of material that is available for dissolution. Work continues on optimizing calibration techniques suitable for very low iron concentrations, and evaluation of the accuracy of the technique and its detectability threshold.

5. Study #2:

Fe and Pb transport during the reactor work cycle

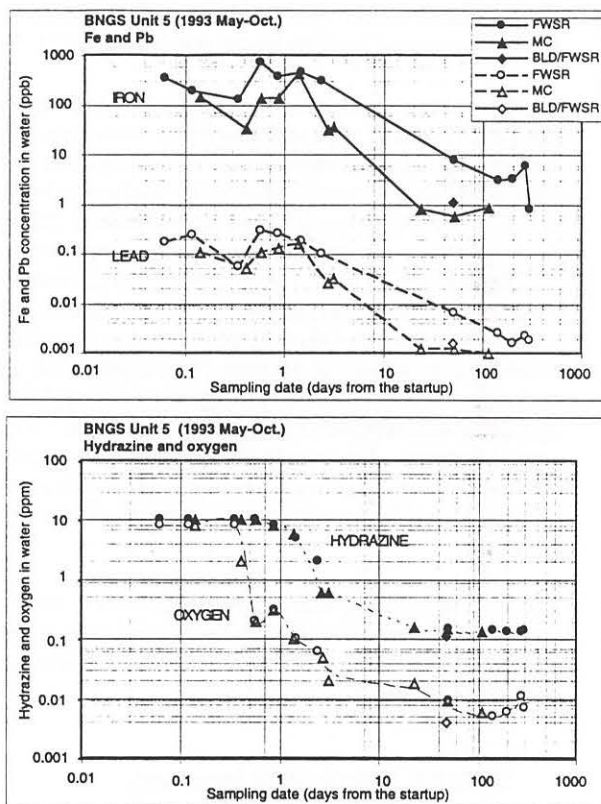


Figure 3. Data on iron and lead concentrations in ppb ($\mu\text{g}/\text{kg H}_2\text{O}$) obtained from XRF measurements of CPT specimens, collected during one reactor cycle in 1993 in Bruce B, Unit 5. The logarithmic scale clearly separates the reactor start-up specimens from steady-state operation specimens. Lead content follows the variation in iron. Similar behaviour was observed in 2 other cycles in Units 6 and 7. Bottom: hydrazine and oxygen contents for the same period.

A series of CPT secondary-side specimens from BNGS Units 5, 6 and 7 were examined. The specimens were collected in 1993 and 1994, in 1- to 2-h sessions

during the first 1 to 2 d after start-up, and then in several 6- or 7-d sessions during several months of the steady-state operation. The specimens were from various sampler locations, including condensate extraction pump (CEP) discharge, feedwater collected locally (using a mobile cart, MC; and at the sampling room, FWSR), and blowdown (BLD) water.

The XRF analyses showed that large amounts of iron are present in the system at start-up (up to 700 ppb); it drops down to ~ 1 ppb range during reactor steady-state operation. Figure 3 shows iron concentration for one startup cycle in Unit 5. (Note the logarithmic scale that clearly separates the start-up data from the steady-state data.) Similar behaviour was also observed in Units 6 and 7. These results are correlated with chemical form of iron measured by Mössbauer spectroscopy [2].

Figure 3 also shows data for lead. Lead concentrations are ~2 to 3 orders of magnitude lower than iron, but interestingly, lead content follows a dependence on iron: high lead content is present at reactor start-up (up to 0.5 ppb), and is much lower during reactor steady-state operation (below 0.1 ppb). More measurements will be performed to verify this result and to observe whether this behaviour is typical for each reactor cycle. Lead monitoring can then be conducted to establish the database for evaluating possible correlations with other parameters of SG chemistry. Figure 3 (bottom) shows hydrazine and oxygen concentrations measured at the same locations. No correlation is observed at start-up, but low iron and lead concentrations during steady-state operation tend to accompany low hydrazine and oxygen contents.

The data in Figure 3 also show that feedwater collected locally (using mobile cart) contained less crud than water in the sampling room. The opposite effect was observed in Unit 7.

6. Study #3: Primary-side specimens

An XRF evaluation of primary-side specimens was performed on 16 primary heat transport (PHT) specimens from DNGS, collected during sampling sessions in 1996 and 1997 (see also [2]). The heavy water is sampled using sampling lines leading from reactor outlet common headers to modified integrated crud samplers installed in each reactor water sampling room. Some data on the specimens, provided by the stations, are given in Table 1, together with selected results of XRF evaluation. One BNGS specimen was also measured. These XRF measurements pose a special challenge because of the interfering effects of radioactive species in the spectra.

Preliminary XRF measurements performed on primary-side specimens show the usefulness of this technique for evaluation of transport of iron and other elements in the primary side. Iron and zirconium were the two main components in all specimens. A number of minor elements were also observed and identified.

Quantitative evaluation provided data on crud levels: they were highest in the February '96 sampling session, and were much lower in the next two sessions.

Mass transport evaluated from XRF measurements is compared with the data obtained by specimen weighing in Table 1 and Figure 4. The ratio between the XRF and weighing data varies from 1 to 7 for various specimens. The consistently higher values obtained from weighing can be explained by the presence of water in the specimens (probably mostly in the substrates), because the radioactive samples are not dried at elevated temperatures. This result indicates that the weighing method used to evaluate the crud level might be inaccurate and that material transport might be lower than originally thought on the basis of filter weighing.

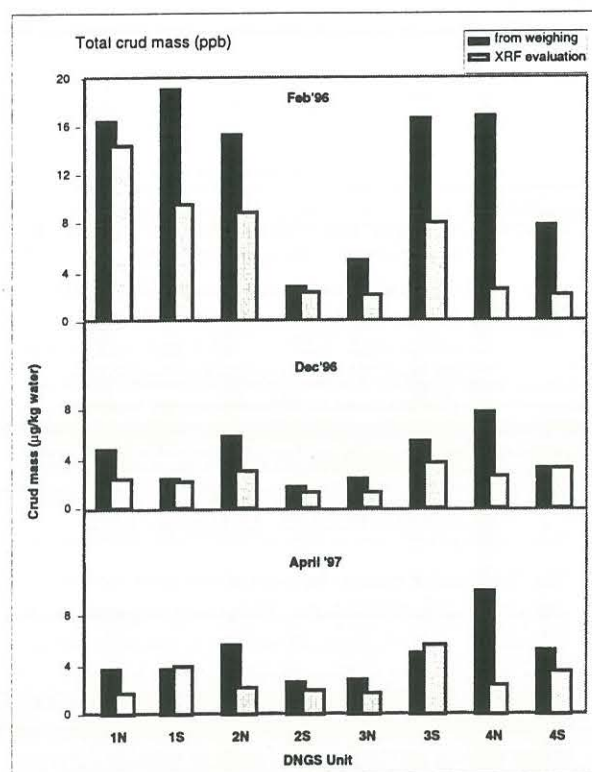


Figure 4. Total mass of particulates (crud mass), calculated from XRF analysis and sample weighing. Measurements concern PHT specimens of 3 recent steady-state sampling sessions (Darlington NGS).

Large amounts of zirconium were present in the specimens from all four DNGS units. Zirconium

content ranged from 5 to 30% of iron, up to 0.6 ppb, see Table 1 and Figure 5. Similarly, a high zirconium fraction (~25%) was also measured in one Bruce B PHT specimen.

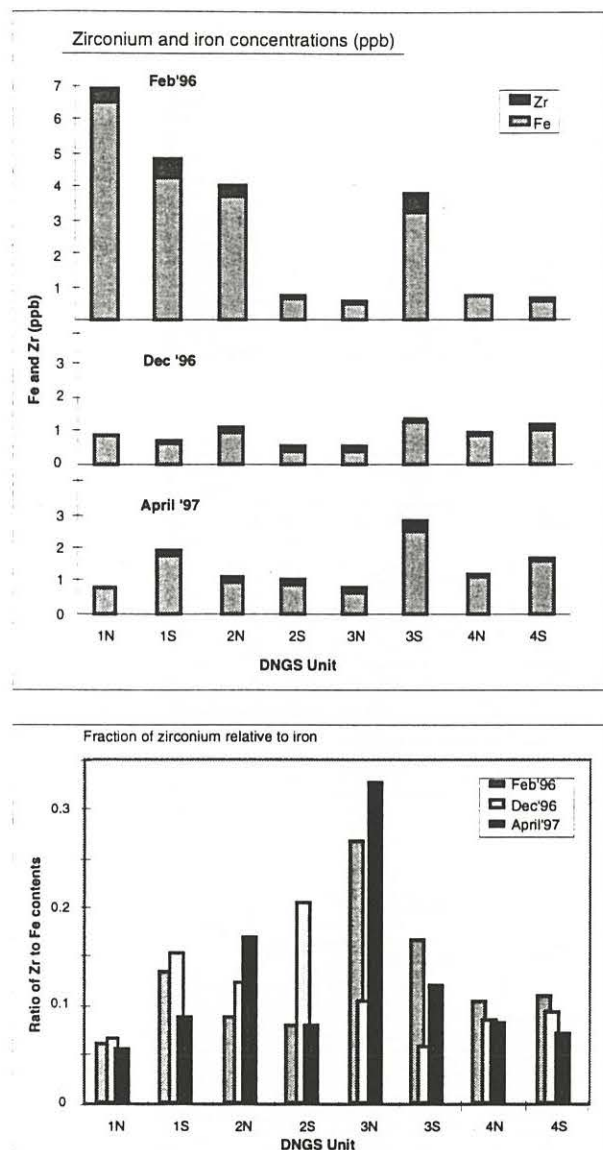


Figure 5. Top: Concentrations of Fe and Zr in crud, as measured from XRF analysis in PHT specimens of 3 recent steady-state sampling sessions (Darlington NGS). Bottom: Ratio of Zr to Fe in the same specimens.

There might be a number of reasons for the presence of zirconium in crud. Zirconium can originate from scratching pressure tube inner surfaces during axial motion of fuel bundles, from fretting at the inlet ends of the pressure tubes by the bearing pads, and from fretting of the Zircaloy-4 bearing pads on fuel sheathing [2]. Apparently the result of wear debris, the presence of zirconium in crud is indicative of fretting and wear, and

possibly of corrosion, of either pressure tubes or nuclear fuel sheaths or both. The identification of what is the main source of zirconium and the quantification of the fraction of zirconium that comes from pressure tubes in comparison with the fraction that is due to fuel, might be performed by analyzing the Nb and Sn contents in crud; such XRF measurements are planned. The data on debris can then be correlated with system chemistry parameters as well as surveillance and oxide thickness data.

Quantitative XRF evaluation of radioactive specimens required correcting the XRF spectra for radioactive species. Figure 6 shows a low-energy spectroscopic emission spectrum compared with an XRF spectrum measured for the same PHT specimen. A number of radioactive species can be identified, including ^{55}Fe , ^{124}Sb and ^{119}Sn . However, because the spectroscopic emission spectrum was measured using a different detector geometry than that of the XRF spectrum, no direct comparison of line amplitudes was possible. Incidentally, the presence of ^{55}Fe in the specimens allowed us to detect chlorine in the XRF analysis.

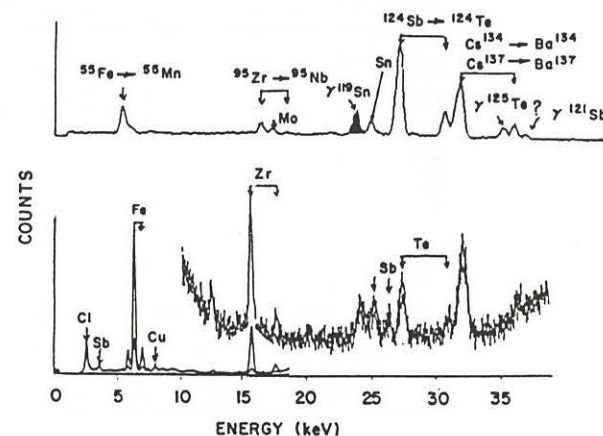


Figure 6. Typical XRF spectra (bottom) and spectroscopic emission spectrum (top) measured for one Darlington PHT specimen. Note a number of emission lines, including ^{55}Fe and ^{119}Sn and ^{124}Sb , as marked. In the XRF spectrum, the main elements are Fe and Zr. Low-energy Cl and Sb lines are observed because of the presence of radioactive ^{55}Fe in the sample.

In this work, quantitative XRF evaluation of radioactive specimens was performed either directly from the spectra or using approximate calibration models. The accuracy was satisfactory for Zr and Fe and several other elements. Accurate measurements for elements such as

Table 1.
XRF and station data on PHT specimens obtained in 3 sampling sessions in DNGS

February '96 Sampling

Unit Loop	XRF data					Station data				Mass ratio: Weighing to XRF
	Fe ppb	Zr ppb	Zr/Fe ratio	Total mass mg	Crud conc. $\mu\text{g/kg}$	pH	Deut.	Weight mg	Crud conc. $\mu\text{g/kg}$	
1N	6.5	0.39	0.06	2.0	14.4	10.58	6.32	2.3	16.4	1.1
1S	4.2	0.57	0.13	2.0	9.6	10.57	6.34	4.0	19.0	2.0
2N	3.7	0.32	0.09	2.9	8.9	10.52	6.24	5.0	15.3	1.7
2S	0.6	0.05	0.08	0.9	2.3	10.54	6.65	1.1	2.9	1.3
3N	0.4	0.12	0.27	0.6	2.2	10.43	5.23	1.4	4.9	2.2
3S	3.2	0.53	0.17	2.7	8.0	10.44	4.98	5.7	16.6	2.1
4N	0.7	0.07	<0.1	0.3	2.5	10.51	5.87	1.8	17.0	6.8
4S	0.5	0.06	<0.1	0.3	2.1	10.51	5.80	1.0	7.9	3.8

December '96 Sampling

Unit Loop	XRF data					Station data				Mass ratio: Weighing to XRF
	Fe ppb	Zr ppb	Zr/Fe ratio	Total mass mg	Crud conc. $\mu\text{g/kg}$	pH	Deut.	Weight mg	Crud conc. $\mu\text{g/kg}$	
1N	1.1	0.07	0.07	0.72	2.5	10.47	4.95	1.4	4.8	2.0
1S	0.9	0.14	0.15	0.56	2.2	10.49	5.00	0.6	2.3	1.0
2N	1.3	0.16	0.12	1.15	3.0	10.26	1.93	2.2	5.8	1.9
2S	0.5	0.11	0.20	0.52	1.3	10.25	2.46	0.7	1.7	1.3
3N	0.5	0.06	0.10	0.30	1.3	10.41	5.57	1.6	2.5	2.0
3S	1.7	0.10	0.06	0.88	3.7	10.41	5.45	1.3	5.5	1.5
4N	1.1	0.10	0.08	0.22	2.5	10.45	4.09	0.7	7.9	3.1
4S	1.5	0.14	0.09	0.20	3.3	10.45	4.23	0.2	3.4	1.0

April '97 Sampling

Unit Loop	XRF Data					Station Data				Mass ratio: Weighing to XRF
	Fe ppb	Zr ppb	Zr/Fe ratio	Total mass mg	Crud conc. $\mu\text{g/kg}$	pH	Deut.	Weight mg	Crud conc. $\mu\text{g/kg}$	
1N	0.8	0.04	0.05	361	1.7	10.42		0.8	3.6	2.8
1S	1.7	0.15	0.09	720	3.9	10.45		0.7	3.8	1.2
2N	0.9	0.16	0.17	706	2.3	10.44		1.8	5.8	3.2
2S	0.9	0.07	0.08	535	2.0	10.43		0.7	2.6	1.6
3N	0.6	0.20	0.33	513	1.7	10.38		0.9	2.9	2.2
3S	2.5	0.30	0.12	2158	5.7	10.47		1.9	5.1	1.1
4N	1.1	0.09	0.08	367	2.5	10.36		1.5	10.2	5.1
4S	1.6	0.11	0.07	1122	3.5	10.36		1.7	5.3	1.9

Nb and Sn (with very low contents and/or overlapping X- and gamma-ray lines) require that corrections for emission lines be incorporated into the analyzer calibration process. To incorporate the appropriate corrections into the deconvolution process and into the calibration models, spectroscopic measurements have to be performed using the same geometry as that used in the XRF measurements. This will be possible after some modifications are made to the XRF analyzer.

7. On-line XRF analysis

There is a movement, led in the United States by the Electric Power Research Institute (EPRI), to develop a system for a quasi-on line iron probe to monitor particulate corrosion products. One system has been successfully tried at a small number of US plants, and a company has been set up to commercialize the units [7]. The unit consists of a flow-cell and a simple XRF analyzer, equipped with proportional counter that is set for Fe analysis. The measurements are to be performed without removing the filter from the sampler, and the sampling system is incorporated into the sample chamber of an XRF analyzer. Water is periodically removed from the sample chamber to permit XRF measurement, and the cycles would be repeated until the particulate loading in the sample chamber warrants a filter change. Because of low detector resolution, the unit provides integrated data on iron and neighbouring elements in the periodic table.

CANDU stations are interested in this technique, and one EPRI-type unit has been purchased for tests. Considerable scrutiny of the on-line work will be required before an actual standard procedure is established for specific station conditions. A number of issues should be addressed. The field analyzer has to be calibrated, its performance and accuracy tested for specific station conditions, and the method of data collection established. Calibration methods and standards developed in the laboratory work on the high resolution analyzer can be used. Line overlap will have some detrimental effect on the accuracy of iron monitoring; however, this is not considered significant because iron is by far the most prominent element in crud. Stabilization of an internal calibration peak amplitude might be critically important because very thin deposits are expected, and the measurement geometry is more difficult to control than in off-line measurements. Whether the system is capable of monitoring elements other than iron remains to be seen, and will need to be tested for individual elements, station conditions and requirements.

The accuracy of iron (and other elements) monitoring will also depend on mass transport in the system because it depends on the amount of material that is

deposited on the filter during each cycle of water flow. At an iron concentration in water of ~ 1 ppb, about 200 μg of particulate material is deposited on a filter during 30 min; and correspondingly, about 20 μg at 0.1 ppb, and 2 mg at 10 ppb. Thus with a 30-min collection time, concentrations below ~ 1 ppb, or even ~ 5 ppb, will be below the detection limit. Sufficiently large iron concentrations are present during reactor start-up to monitor iron in a quantitative way. During steady-state reactor operation, when there is low material transport, on-line iron monitoring might be performed in a "digital mode"; i.e., small amounts of deposits will be collected during 15- to 60-min intervals -- at normal conditions -- undetectable (digital 0); however, a sudden "burst" of the material will be recorded (digital 1). Alternatively, longer collection times might be used. Exact detection limits have to be evaluated and determined. The high resolution analyzer should serve as a check for performance of the on-line unit. It can be also be periodically used in on-line measurements (e.g., when monitoring elements other than iron or when high accuracy for iron is needed).

8. Summary and conclusions

- Sampling of corrosion products in both primary and secondary sides of CANDU stations is important to establish and control chemistry specifications and practices. Evaluation of CPT specimens obtained from integrated CPT samplers installed at the stations helps to better understand corrosion transport phenomena, which are important in many areas of reactor operation, including corrosion of feeder pipes, fouling of SGs, length of outages, reactor-inlet header temperature limits, frequency of chemical cleaning, radioactive waste, etc.
- The XRF method is being developed to nondestructively determine elemental composition and mass of CPT specimens collected as filtered deposits. Elemental analysis is one basic method of CPT specimen evaluation; it complements other methods, including Mössbauer spectroscopy, X-ray diffraction analysis and electron microscopy [1].
- The XRF method offers the following benefits in comparison to wet chemistry methods:
 - nondestructive analysis;
 - rapid analytical response and turnaround;
 - lower analysis cost (no digestive step is needed);
 - no active waste (in case of PHT specimens);
 - possible on-site use and potential for (quasi) on-line analysis;
 - possibility of storing and re-analyzing analytical data (e.g., to identify additional elements).

- Measurements performed on samples of CPT specimens showed that the XRF accuracy for iron can be comparable to that of laboratory-based wet chemistry methods. This must be verified for a larger range of specimens, various concentration ranges and station sampling conditions. The method was shown to work on small amounts of material ($\sim 10 \mu\text{g}/\text{cm}^2$ or $\sim 100 \mu\text{g}$ per filter, possibly less).
- In addition to iron analysis and monitoring, the XRF technique is suitable for measuring a wide range of other elements. Work on high-accuracy nondestructive analysis of elements other than Fe in CPT specimens is in progress. Elements of interest can include Ni, Cu, Zn, and Pb in secondary-side water and Fe, Zr, Sn, Sb, and Cl in primary-side water.
- Data on crud transport and composition were obtained. In secondary-side water, large iron transport is observed at reactor start-up, and it is at ~ 1 ppb level during steady-state operation. Lead content tracks that for iron (high at start-up, lower during steady-state operation), at the level of ~ 0.1 ppb. In primary-side water, large zirconium fractions (5 to 30%) were observed in addition to iron. The measurements are correlated with the system chemistry parameters in Reference [2].
- These data indicate that the XRF method can be suitable for analysis of primary side specimens. Accurate analysis for other elements will be performed to identify the main source of zirconium in the system; to define the fraction of zirconium that comes from pressure tubes in comparison with the fraction that is due to fuel.
- All measurements described in this work were performed using a portable XRF analyzer, featuring recent technological advances. The analyzer has shown to be a useful and versatile tool, providing laboratory-quality analytical capability in a portable instrument. Methods are under development to optimize this analyzer for high-accuracy measurements on thin films.
- Because of the need for decreasing costs and improving accuracy, there is a growing tendency throughout the analytical community to bring the analytical method to the site rather than to take samples in the field and bring them to the laboratory. The XRF method can also be used for quasi on-line monitoring performed under operating conditions by combining the XRF analyzer with a flow cell. There is a possibility of extending on-line monitoring to elements other than iron.

However, the use of the field instrument for on-line measurements needs considerable scrutiny, before a standard procedure can be established for station-specific conditions.

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References

1. J.A. Sawicki, M.E. Brett, R.L. Tapping, Position Paper on Secondary-Side Corrosion-Product Transport and Oxidation State, Atomic Energy of Canada Limited Report, COG-96-482, RC-1709.
2. J.A. Sawicki, M. Dymarski, B.D. Sawicka, "Primary Side Crud Sampling and Characterization: How it may help to better maintain CANDU reactors", these proceedings.
3. B.D. Sawicka, "XRF Method for Analysis of Filter Deposits", In Proceedings of the Second CANDU Chemists Workshop, Toronto, 1996 September 16-17.
4. B.D. Sawicka, "XRF Analysis of CPT Specimens from Darlington Unit 2. Comparison of XRF and ICP Methods for Fe analysis", Atomic Energy of Canada Limited Report, COG-97-300, 1997 July.
5. B.D. Sawicka, "Determination of Corrosion Products by XRF", invited talk presented at the On-line Analyzer Users Group Meeting, Darlington NGS, 1997 June 12.
6. S. Piorek, "Modern, PC based, High Resolution Portable EDXRF Analyzer Offers Laboratory Performance for Field, In-situ Analysis of Environmental Contaminants", Nuclear Instruments and Methods in Physics Research A 353 (1994) 528-533.
7. D. Connolly and P. Millett, "On-line Particulate Iron X-ray Monitor", Ultrapure Water Journal, February 1994.