ANALYSIS OF CORROSION-PRODUCT TRANSPORT USING NONDESTRUCTIVE XRF AND MS TECHNIQUES

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ABSTRACT

This paper describes the application of X-ray fluorescence (XRF) and Mössbauer spectroscopy (MS) techniques to monitor corrosion-product transport (CPT) in water circuits of nuclear reactors. The combination of XRF and MS techniques was applied in studies of CPT crud filters from both primary- and secondary-side water circuits (i.e., radioactive and nonradioactive specimens) of CANDU® reactors. The XRF-MS method allows nondestructive analysis of species collected on filters and provides more complete information about corrosion products than commonly used digestive methods of chemical analysis. Recent analyses of CPT specimens from the Darlington Nuclear Generating Station (NGS) primary side and the Bruce B NGS feedwater system are shown as examples. Some characteristics of primary and secondary water circuits are discussed using these new data.

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1. INTRODUCTION

Sampling and characterization of corrosion products provide information on corrosion and corrosion-product transport (CPT) in water circuits of nuclear reactors. Systematic evaluation of CPT is an important task for both primary- and secondary-side water circuits of CANDU stations. It relates to fouling of steam generators, corrosion of feeder pipes, an increase in reactor-inlet header temperature, frequency of cleaning, exposure of personnel to radiation fields, maintenance costs, etc. [1, 2]. Sampling of CPT is performed by collecting specimens on filters in specially installed integrating samplers. Depending on the type of filters used, particulate or ion-exchange, either suspended solids ("crud") or soluble species are extracted from circulating water. After the filters are removed from the samplers, the deposits are usually analyzed off-line using digestive methods of chemical analysis.

We discuss here progress in evaluation of CPT filters using X-ray fluorescence (XRF) and Mössbauer spectroscopy (MS). These techniques provide nondestructive means of analysis, which permits the filters to be retained for further studies or for future reference. They also provide more complete information about corrosion products than commonly used digestive chemical methods. The application of XRF and MS methods for both primary (radioactive) and secondary (nonradioactive) side filters was evaluated using samples from Darlington and Bruce B Nuclear Generating Station (NGS).

2. EXPERIMENTAL

X-Ray Fluorescence

The development of XRF technique for quantitative elemental analysis of thin filter deposits is presented in detail in Reference 3. The XRF technique offers a valuable alternative to digestive methods of elemental analysis of CPT specimens. In addition to being nondestructive, XRF is faster than digestive methods because no digestive step is needed and because simultaneous analysis for various elements is performed in one step. On CPT specimens, XRF was shown to be capable of determining and measuring elements such as iron and lead, with an accuracy comparable to that of optical emission spectroscopy of dissolved samples. Other elements recorded in CPT specimens included Ni, Cu, Zn, Mn, and Ti in both primary- and secondary-side specimens, as well as Zr, Sn, Sb, Cl, and some heavy elements in primary-side specimens. The filter substrate usually has a negligible effect on XRF results.

XRF analysis is performed by measuring X-ray emission spectra and identifying atomic transitions characteristic of the elements present in the sample. The accuracy of XRF depends on many factors, including the quantity of material available for analysis as well as its form and geometry. In this work, a portable, energy-dispersive XRF analyzer X-MET 920 [4] was used, in which X-rays are detected using a LN_2-cooled Si(Li) detector of high resolution (0.17 keV for the Mn $K\alpha$ line at 5.9 keV), and the process of data collection and analysis is microprocessor-controlled. Using two radioactive sources, 20 mCi ^{109}Cd and 10 mCi ^{241}Am, the analyzer is capable of measuring elements ranging in atomic number from titanium to uranium. XRF spectra obtained using 22 to 25 keV X-ray photons of ^{109}Cd can show well-resolved fluorescence lines for elements such as Fe, Ti, Ni, Cu, Zn, Zr, Nb, Pb and others. By using ^{241}Am 59.4 keV γ-photons, one can measure elements that have high atomic numbers, e.g., Sn, Sb and actinides. Alternatively, an ^{55}Fe source of 5.9 keV photons can be installed to measure elements with low atomic numbers, including Cl. Analysis can be performed over the user-selected area, up to the size of the detector window (i.e., circular area of 5 cm^2, 25 mm in diameter).

In all tests described here, 0.45-µm pore-sized acetate membrane filters were used. The deposited area was circular and varied from 9 to 11.5 cm^2 (34 to 38 mm in diameter). In all measurements reported here, the readings were averaged over an area of 5 cm^2, which equals about half the deposit area.

XRF analysis of specimen composition is based on a correlation between the amplitude of characteristic X-ray lines and element concentration. Approximate quantitative analysis can be performed directly from the measured spectra: the amplitude ratio of corresponding lines corrected for background and excitation factors can give an approximate ratio of corresponding elements. Accurate quantitative analysis is performed using semiempirical calibration programs, which are developed for a specific type of study and experimental conditions, including specimen characteristics and geometry, analysis range, interfering elements, etc. The models are based on measurements performed on suitable calibration standards; the measured calibration spectra are then used to calculate calibration equations for individual elements, after preliminary evaluation has been performed by computer to implement corrections for various geometrical and physical effects. For primary-side specimens, the presence of radioactive species in the analyzed specimens also has to be taken into account. For accurate quantitative analysis of small quantities of material, often less than 10 µg/cm^2, a suitable set of standards and the construction of the calibration models are critically important. This work is now in progress. Fig. 1 shows examples of the measured spectra.

Mass transport can be evaluated from XRF measurements by calculating total concentrations of all measured elements and adding corrections for the chemical form of crud (oxides) and the presence of light elements that are not measured (lithium). Total crud levels in µg per kg water (ppb) are next calculated by normalizing the measured data to the mass of the flow water that circulated during collection of crud on the filter. This method is thought to be more accurate than weighing filters and calculating the mass gain, which is often used to calculate CPT in primary-side water.

Mössbauer Spectroscopy

Mössbauer spectroscopy provides a unique method of examining the chemical form of iron in very thin layers of filtered deposits, ~10 μg Fe/cm^2. The oxides, such as magnetite (Fe_3O_4), hematite (α-Fe_2O_3), goethite (α-FeOOH), lepidocrocite (γ-FeOOH), which are most frequently encountered in all-ferrous water systems, as well as metallic iron or carbon steel particles (α-Fe), can be readily determined from the MS spectra. The presence of a high fraction of magnetite in feedwater and steam generator blowdown, as well as in the primary-heat-transport system, is indicative of reducing water chemistry in CANDU carbon steel piping; because of that, the magnetite fraction is becoming one of the control parameters. The presence of other (reducible) oxides can indicate oxygen in-leakage and excessive corrosion processes occurring in the system.

MS transmission spectra were obtained at room temperature using a 50 mCi ^{57}CoRh source of 14.4 keV γ-rays and a Kr-CO_2 proportional counter. The absorbers consisted of the whole deposit material, and hence the spectra represented the integrated effect over the total material collected on each filter. Because of their low atomic mass and low γ-ray absorption, the acetate substrates had a negligible effect on the MS measurements. Different chemical forms of iron can be recognized in the spectra by their characteristically different multiplets of lines, parametrized by isomer shift, quadrupole splitting, and hyperfine magnetic splitting of individual multiplets. Spectral components that correspond to various iron forms are extracted from the measured spectrum by deconvolution using a least-squares fitting procedure. The relative spectral areas of various components give a measure of concentrations of corresponding forms of iron. Measurements at various temperatures are sometimes needed to help in spectra deconvolution and interpretation. Information about elemental composition of the deposits, acquired by XRF before MS measurement, is also very helpful in this analysis.

3. PRIMARY-SIDE SPECIMENS

In the past, primary-side crud filters were only sporadically used in CANDU reactors. In 1996, chemists at Darlington NGS started collecting primary-side specimens at regular 3 month intervals; the specimens are collected at the reactor outlet headers of Units 1 to 4, in both North and South loops. The filters are dried at room-temperature and weighed at the station to get an approximate total mass gain. The XRF and MS analyses are being performed at the Chalk River Laboratories of AECL. By regular sampling and XRF-MS analyses, a systematic database is being developed to correlate the iron crud transport and iron oxides content with primary-side chemistry and operational procedures.

The data for 1996 February, 1996 December and 1997 April samplings are discussed here as an example. The samples contained a number of radionuclides that were identified using a wide-energy (< 2 MeV) Ge(Li) spectrometer: ^{60}Co, ^{95}Zr, ^{95}Nb, ^{106}Ru, ^{124}Sb, ^{131}I, ^{134}Cs, ^{137}Cs, and others. The wide-range Ge(Li) spectrometers commonly used at stations are not capable of identifying low-energy emitters. The latter, such as 5.9 keV X-rays of ^{55}Fe and 23.9 keV γ-rays of ^{119}Sn, were determined using our low-energy (<30 keV) detector equipped with a thin beryllium window, and set selectively for low-energy range. An example of such low-energy emission spectrum is shown in Figure 1 (top). The XRF spectrum obtained for the same specimen is shown in Figure 1 (middle). The presence of radionuclides in the specimens is a major complication in XRF analysis of radioactive primary-side filters. The methodology is being developed to properly account for the contribution of radionuclides to XRF spectra. It is interesting to note that, because of the presence of radioactive ^{55}Fe in the specimens, we also measured in the XRF spectra some low-energy X-rays that would otherwise not be excited; these included the 2.6-keV K-line of Cl (present in Darlington NGS specimens collected during February 1996 sampling), and the 3.6 keV L-line of Sb.

Results of XRF analyses of all the specimens showed that, of the elements identified, concentrations of iron and zirconium were always the highest; a number of minor elements were also identified, including Cu, Ni, Zn, Sn, Sb, Te and Ba. The fraction of zirconium in different units and loops varied from below 5 % to as high as 30 % of iron content, as shown in Figure 2. The highest concentration of zirconium was observed in Unit 3N. In early sampling sessions, the concentrations of iron measured were up to ~10 ppb (μg per kg D_2O); high iron levels observed in Units 1, 2N and 3S in 1996 February, decreased markedly during later sampling sessions. Crud levels were systematically lower for Unit 4 (Table 1). As shown by recent 1997 April session XRF data, in well-controlled, steady-state reactor operation, iron concentration can be as low as ~3 ppb and zirconium concentration at ~0.1 ppb (Figure 2 and Table 1).

The scanning electron microscopy-energy dispersive X-ray (SEM/EDX) analysis of filter deposits showed that although iron was present in very fine, approximately micron-sized particles, zirconium was often in a form of 10 to 30 μm particles. Zirconium in the crud can originate from Zr-2.5Nb pressure tube oxide spalling, from scratch marks on the inner tube surfaces during axial motion of fuel bundles, from fret marks at the inlet ends of the pressure tubes caused by the bearing pads, and from fretting of Zircaloy-4 bearing pads on fuel bundles. The mass of zirconium in the crud should be correlated with these wear effects. Further systematic monitoring of zirconium in the crud should help to identify its main sources. The fraction of zirconium that comes from pressure tubes in comparison to the fraction due to fuel bundles, could be identified by measuring exact quantities of niobium and tin; the XRF method might provide sufficient accuracy to be used for such an evaluation.

The results of MS analyses of these same filter deposits are described in detail in Reference 2. The analyses showed iron mostly as magnetite; however, fractions of reducible iron Fe(III) oxides (hematite, goethite and lepidocrocite) were often much higher than expected in lithiated water under reducing conditions. The observations of excessive reducible iron oxides helped to eliminate oxygen in-leakage and indicated the need of nitrogen blanketing during system lay-ups.

It is important to note that crud transport in primary-side water is thus far obtained by weighing the collected filter specimens and calculating the weight gain. According to our observations, this method may be susceptible to large errors. As shown in Table 1, crud concentrations obtained by weighing filters were equal to the values obtained from XRF analysis in 40% of the cases, they were up to 2 times higher in close to 40% of the cases, and in 25% of the cases they were much higher (up to 7 times in one case). The consistently higher values obtained from weighing filters may indicate that the process of drying filters at room temperature is insufficient to totally remove water from microporous substrates (radioactive samples are not dried at elevated temperatures for the risk of spreaded contamination). Consequently, crud transport in the Darlington NGS primary-side might be lower than previously estimated on the basis of weighing filters.

4. SECONDARY-SIDE SPECIMENS

The study presented here was performed using crud filters collected at Bruce B NGS Unit 5 between May and October 1993, at Unit 6 between February and April 1993 and at Unit 7 between May and July 1994. More than 70 specimens obtained from condensate extraction pump (CEP) discharge, feedwater (collected in sampling room, FWSR, and using a mobile cart, FWMC) and blowdown (BLD) were analyzed. Fig. 1 (bottom) shows XRF spectrum measured for one of the specimens. The concentrations of iron and lead, as well as contributions of various iron oxides were determined. The results are summarized in Figures 3, 4 and 5, together with the data on dissolved O_2 and N_2H_4 concentrations, measured in the same time period as the CPT sampling.

Top left-hand graphs in Figures 3 to 5 show iron and lead concentrations in ppb (µg/kg H_2O) obtained from XRF measurements. In all units, the reactor startup specimens clearly differ from the steady-state operation specimens; in all 4 startups studied, large amounts of iron are observed at reactor startup (up to 700 ppb), dropping down to ~1 ppb range during reactor steady-state operation. Lead was found to vary similarly to iron, but at contents ~2 to 3 orders of magnitude lower than iron.

The time dependence of various chemically different fractions of iron, shown in the right-hand graphs of Figures 3 to 5, indicates that the ratio between iron chemical forms during startups varies greatly from unit to unit. For example, whereas in Units 5 and 7 iron was mostly in the form of magnetite, in Unit 6 it was mostly in the form of goethite (during reactor startup) and hematite (at steady state). The presence of a high fraction of magnetite in feedwater and steam generator blowdown is a good indicator of correct secondary-side water chemistry; the presence of reducible oxides can indicate that increased corrosion processes are occurring in the system.

Concentrations of oxygen dissolved in condensate and hydrazine in feedwater are important chemical control parameters of the secondary water system in Ontario Hydro CANDU reactors. A comparison of oxidation state of steady-state corrosion products in CANDU and pressurized-water reactors (PWRs) shows that, at identical feedwater N_2H_4 to condensate O_2 ratios, the fractions of magnetite in feedwater and blowdown can be markedly lower in CANDU reactors than in PWRs. In Ontario Hydro reactors, hydrazine is used extensively during lay-ups for corrosion protection of steam generators (50 to 200 ppm N_2H_4 is used); hydrazine is an oxygen scavenger and reducing agent in feedwater during reactor startups (~ppm) and steady-state operation (~100 ppb). However, because hydrazine emissions cause environmental and health concerns, there is a desire to limit its use. The highest emissions of hydrazine occur during reactor startups. Reactor startups are also a major contributor of oxidized iron species in CANDU feedwater. Our present studies of the CPT and oxidation state of corrosion products as a function of oxygen level and hydrazine application during both reactor startup and steady-state operation are aimed at minimizing hydrazine usage.

The results show that the content of magnetite depends on the mode of hydrazine application during reactor startup and on the startup mode. Figure 3 shows a study of a slow startup, with low hydrazine levels; the MS phase analysis indicates a low magnetite fraction and larger fractions of more oxidized iron species. In contrast, Figure 5 shows a fast reactor startup with high hydrazine levels that is accompanied by iron mostly as magnetite, with lower contents of other forms of iron. However, when comparing data on iron concentration with changing hydrazine and oxygen concentrations during one reactor startup, one concludes that in some ranges, low iron and lead concentrations tend to accompany low oxygen and low hydrazine contents. The observations lead us to suggest that while sufficiently high hydrazine content is needed to limit oxygen level and to stabilize high magnetite fractions, too high hydrazine content seems to have a detrimental effect, causing more total crud.

The examples of reactor startups examined at the Bruce B NGS show that there is a possibility to fine-tune hydrazine dosage at reactor startup and thus obtain a lower transport of reducible iron species at lower hydrazine usage. However, a larger database is needed to validate these observations and draw further conclusions and correlations.

5. SUMMARY AND CONCLUDING REMARKS

Evaluation of corrosion products from primary and secondary reactor water circuits can benefit from applying the XRF and MS techniques of analysis. Both techniques are nondestructive, which permits retention of the specimens for further studies and for future reference.

The XRF technique offers a useful alternative to digestive methods of elemental analysis. It was shown to be a suitable method for elemental analysis of CPT in both primary and secondary water circuits of CANDU reactors. In addition to being nondestructive, it is also faster than digestive methods, because no digestive step is needed and because simultaneous analysis for various elements is performed in one step. Total mass transport can be measured using XRF, which may offer a more accurate measurement of primary-side specimens than the weighing method. In addition to iron, XRF also permits us to measure the quantity of lead and other elements transported with the water. Portability of XRF instruments permits the analysis to be performed at stations; a quasi on-line analysis is also possible.

Mössbauer spectroscopy provides a unique method of evaluating the chemical form of iron, i.e., iron oxidation states; the presence of various iron species, such as magnetite, hematite, lepidocrocite, etc., can be identified and their relative fractions can be measured.

The combination of both techniques provides information that can be used to establish correlations with water chemistry and that can serve as a diagnostic measure for optimization of system performance. In particular, by combining the results of XRF elemental and MS phase analyses, we obtained quantitative data on various iron species transported to the steam generators during reactor startups and steady-state operation. These data can be used by the stations as an indicator of system chemistry and corrosion. They also provide a database for establishing correlations with other chemical parameters of the water circuits (including pH, oxygen and hydrazine levels, etc.) and to draw conclusions about possible limitation of corrosion/wear rates.

To be useful for CPT monitoring, both the XRF and MS techniques had to be *significantly* improved, relative to their standard use, to ensure high enough accuracy for very small quantities of solids collected on filters.

ACKNOWLEDGMENTS

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TABLE 1

Data on crud concentration (μg/kg) obtained in 3 sampling sessions at the Darlington NGS. Results obtained from an XRF evaluation are compared with data obtained by specimen weighing.

Unit Loop	Crud concentration (μg/kg) from XRF measurements			Crud concentration (μg/kg) from weighing		
	February 1996	December 1996	April 1997	February 1996	December 1996	April 1997
1 N	14.4	2.5	1.7	16.4	4.8	3.6
1 S	9.6	2.2	3.9	19.0	2.3	3.8
2 N	8.9	3.0	2.3	15.3	5.8	5.8
2 S	2.3	1.3	2.0	2.9	1.7	2.6
3 N	2.2	1.3	1.7	4.9	2.5	2.9
3 S	8.0	3.7	5.7	16.6	5.5	5.1
4 N	2.5	2.5	2.5	17.0	7.9	10.2
4 S	2.1	3.3	3.5	7.9	3.4	5.3

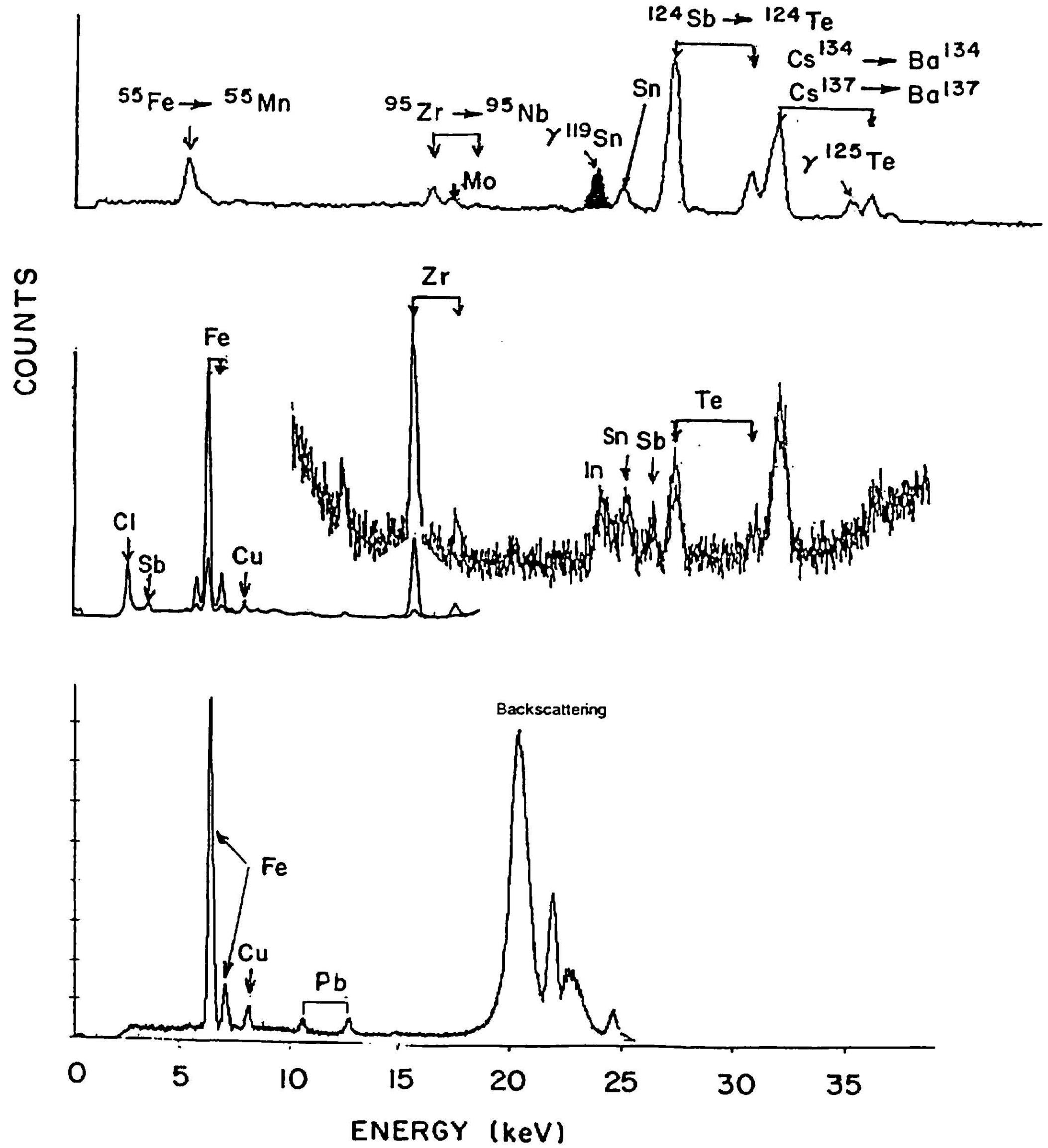
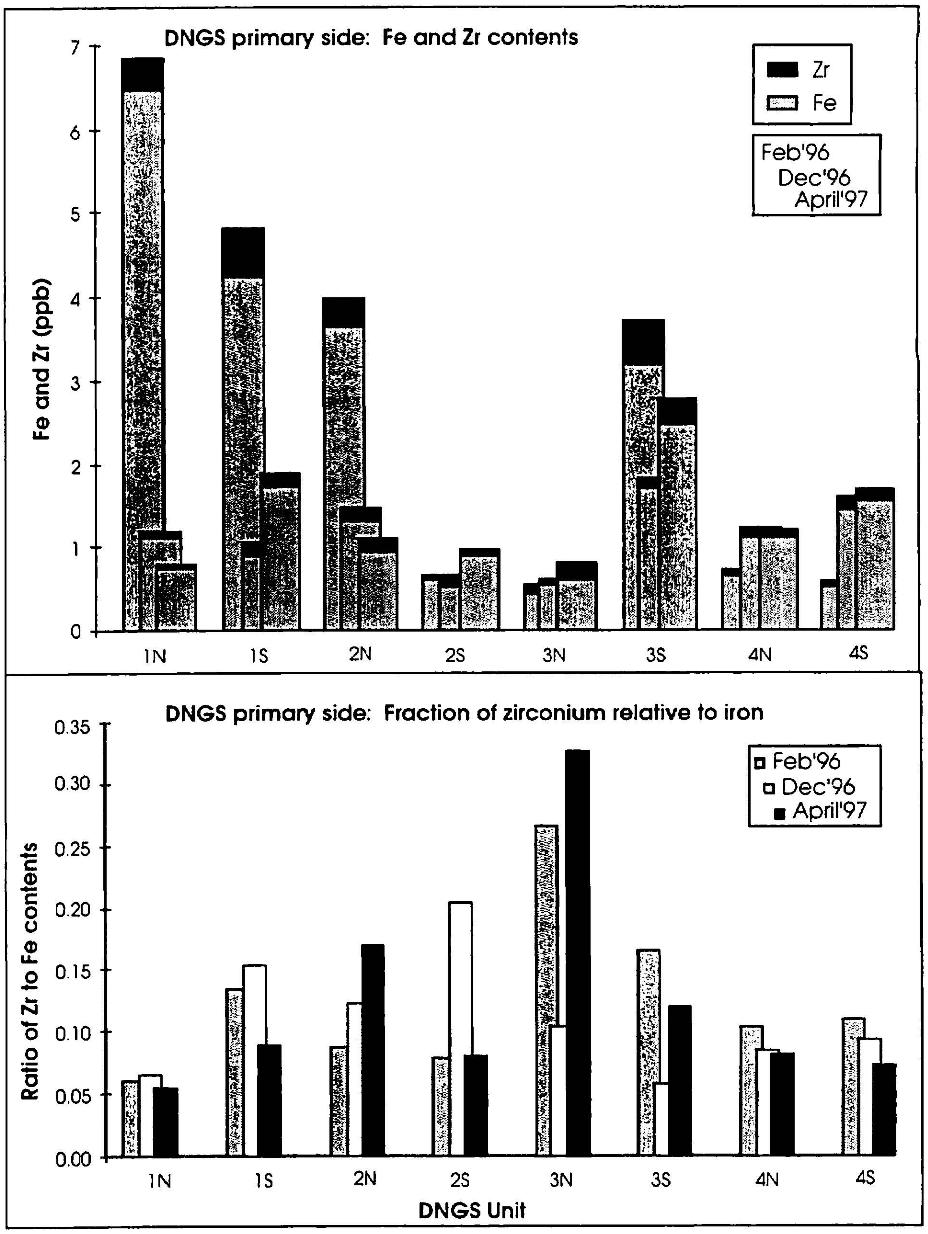


Figure 1. Top: X-ray and γ-ray emission spectrum for one of Darlington NGS primary-side specimens. Middle: XRF spectrum obtained for the same specimen. Note a large-amplitude 17.6 keV Zr line in the XRF spectrum. Bottom: XRF spectrum for one of secondary-side specimens.



DNGS primary side: Fe and Zr contents

DNGS primary side: Fraction of zirconium relative to iron

Figure 2. Concentrations of iron and zirconium in coolant, obtained from XRF analysis of Darlington NGS primary specimens collected in 3 sampling sessions in 1996 and 1997 (top). The ratio of Zr to Fe in the same specimens (bottom).

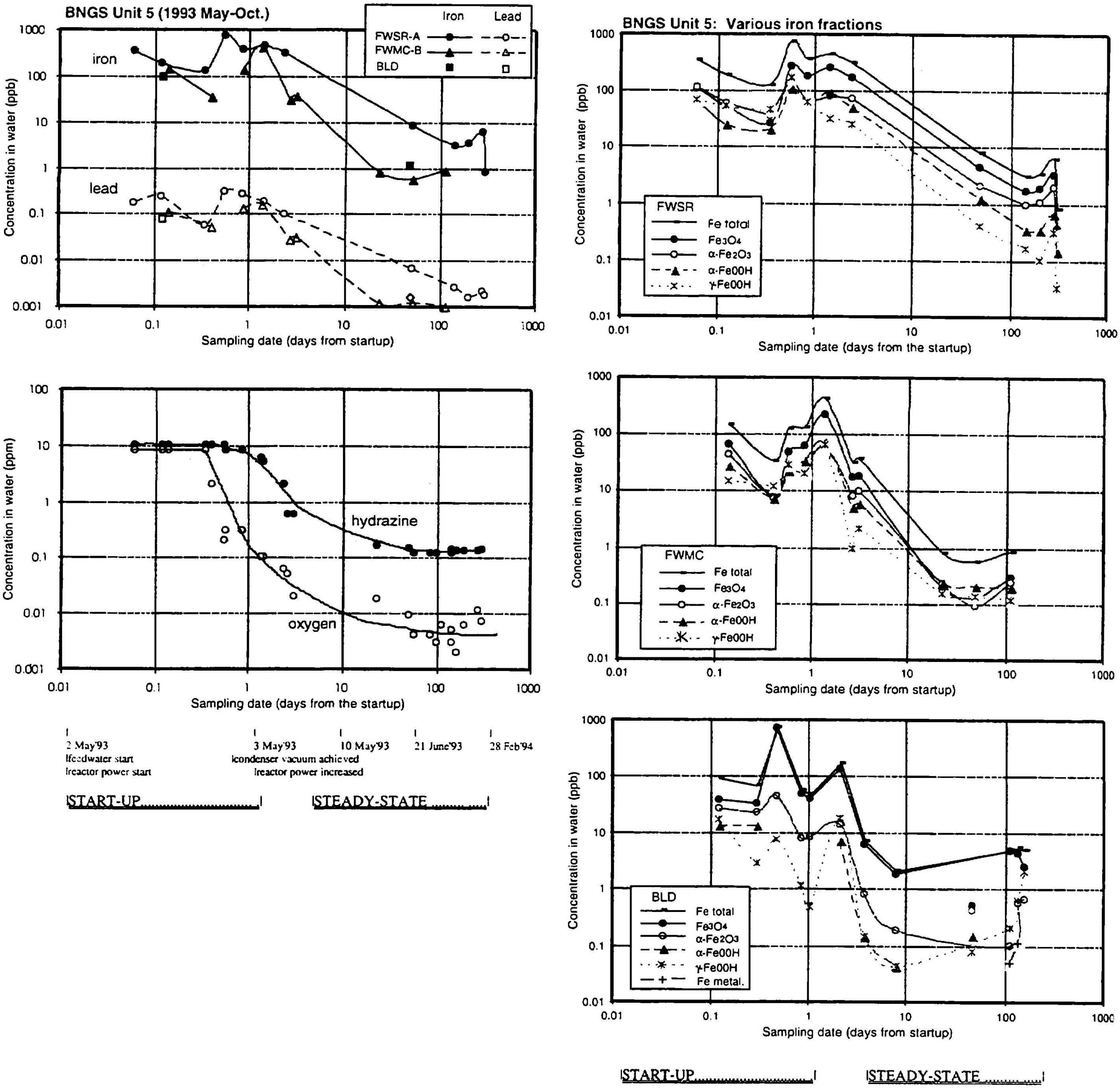


Figure 3. Concentrations of iron and lead (left, top), as well as concentrations of various iron oxides (right) obtained from XRF and MS analyses of secondary-side specimens collected in Bruce B NGS Unit 5 between May and October 1993 (FWSR, FWMC, and BLD). The feedwater hydrazine and condensate oxygen concentrations in the same period are given for comparison (left, bottom).

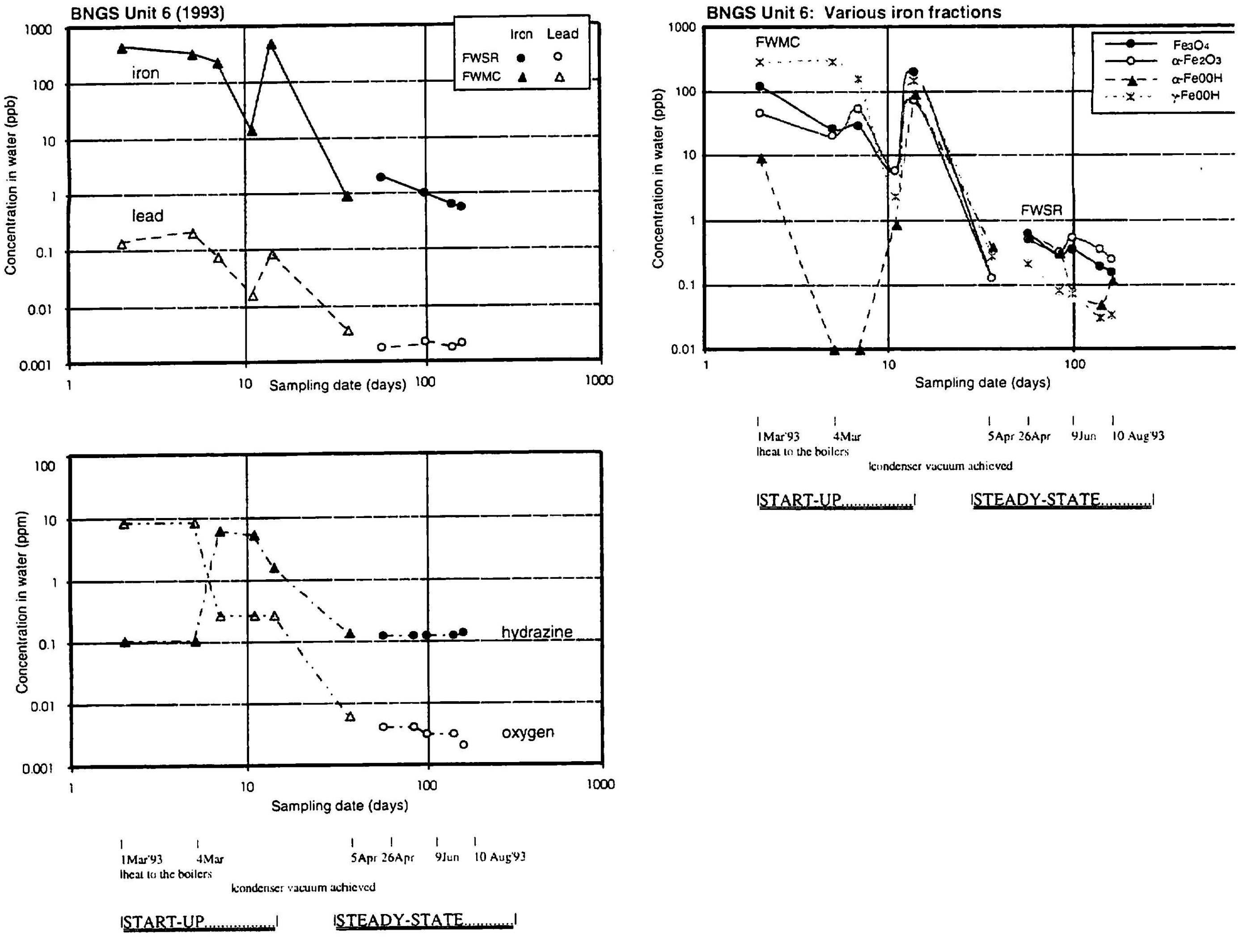


Figure 4. Concentrations of iron and lead (left, top), as well as concentrations of various iron oxides (right) obtained from XRF and MS analyses of secondary-side specimens collected in Bruce B NGS Unit 6 between February and April 1993 (FWSR and FWMC). The feedwater hydrazine and condensate oxygen concentrations in the same period are given for comparison (left, bottom).

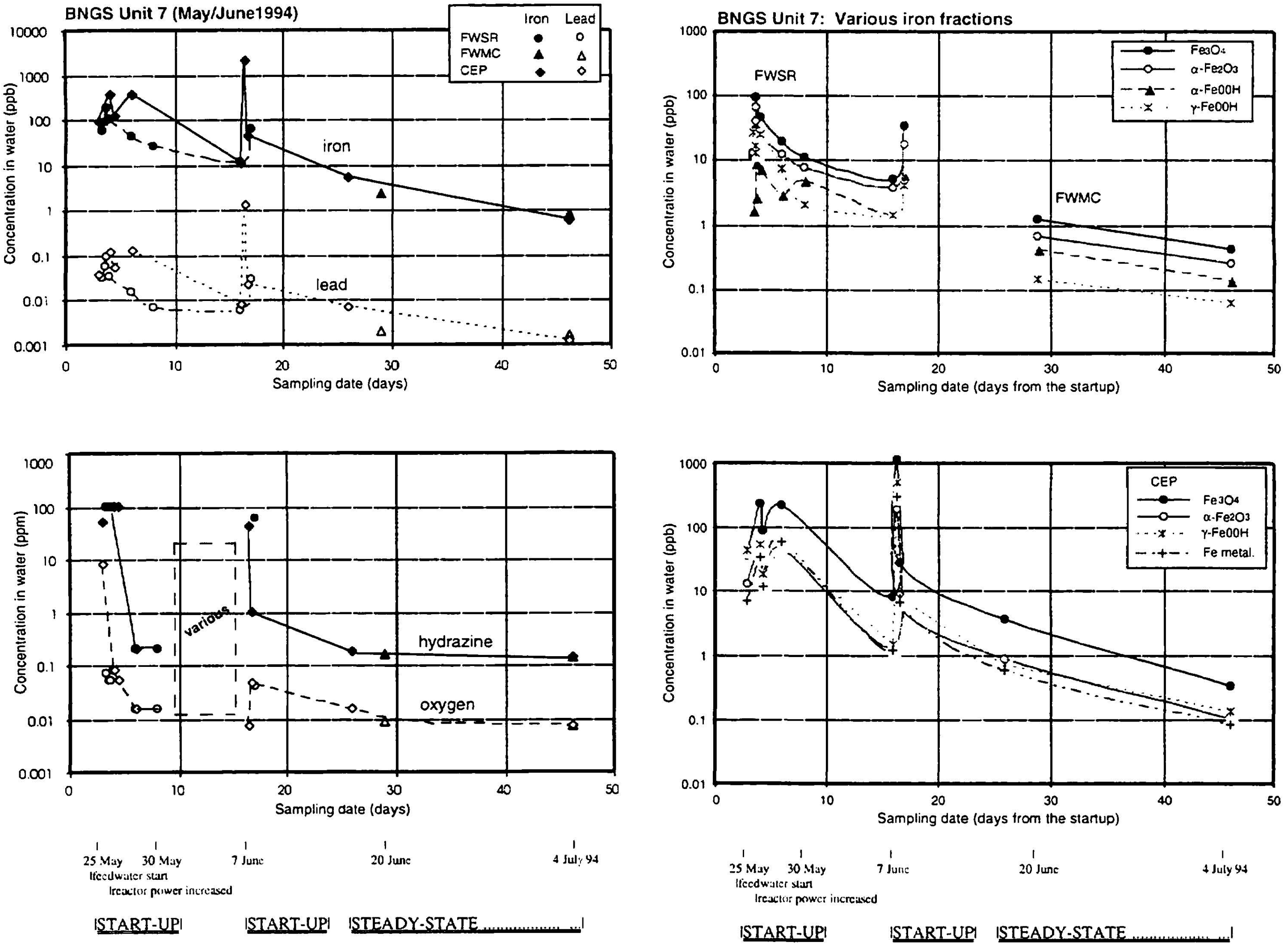


Figure 5. Concentrations of iron and lead (left, top) , as well as concentrations of iron species (right) obtained from XRF and MS analyses of secondary-side specimens collected in Bruce B NGS Unit 7 between May and July 1994 (FWSR, FWMC, and CEP). The feedwater hydrazine and condensate oxygen concentrations in the same period are given for comparison (left, bottom).