

Sampling Considerations for Monitoring Corrosion Products in the Reactor Coolant System in Pressurized Water Reactors



Technical Report

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Sampling Considerations for Monitoring Corrosion Products in the Reactor Coolant System in Pressurized Water Reactors

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REPORT SUMMARY

Chemistry sampling of the reactor coolant system (RCS) of pressurized water reactors (PWRs) can provide significant information regarding the health of the primary system. Timely detection of increased corrosion product concentrations will aid in evaluating any risks associated with the onset of an axial offset anomaly, increased shutdown releases, increased out-of-core dose rates, or increased personnel doses. This report provides recommendations for improved RCS sampling.

Background

Pressurized water reactors do not have a standard requirement to measure reactor coolant system corrosion product concentrations during normal operation, other than that associated with the standard technical specifications for \overline{E} , the average disintegration energy. Instead, a variety of plant-specific sampling practices have evolved that are dependent on the manpower available and the staff's interest in sampling the RCS for corrosion product activity. In general, corrosion product measurements are given a low priority, but the growing problems associated with formation of crud on the fuel means that greater emphasis needs to be placed on obtaining representative corrosion product measurements. These measurements will then indicate the onset of plant problems, particularly those associated with increases in the particulate burden in the RCS.

Objectives

- To provide an historical review of sampling technology literature to illustrate the potential caveats inherent in interpreting data obtained using many current sampling systems.
- To describe examples of normal "grab" sampling methods and alternative methods in use at some plants to improve reliance on RCS corrosion product data.

Approach

Two sample points are normally used for primary coolant corrosion product analysis in Westinghouse and Combustion Engineering (CE) PWRs. These are the RCS hot leg and the chemical and volume control system (CVCS) letdown line, although an RCS cold leg sample point also may be available in some plants. Babcock & Wilcox (B&W) PWRs use one of the RCS cold legs for the reactor coolant sample. The project team evaluated corrosion product sampling methods and data at a number of PWRs. To determine optimal sampling recommendations for obtaining reliable and reproducible RCS data, the team evaluated data quality in context with the sampling location, method, and protocol.

Results

Measuring representative corrosion product concentrations in the RCS is a particularly difficult task. Measurements are fraught with problems due to the way species interact with oxides on the sample line walls and the way pH and corrosion product solubility change as coolant flows along the sample line. Despite the many problems obtaining a representative corrosion product sample from an RCS hot or cold leg, successful measurements should still be possible. For successful measurements to occur, a practicable requirement for making successful and meaningful measurements must exist; one such requirement is offered in this report.

Due to difficulties that exist in PWRs that cannot use a continuously flowing RCS hot or cold leg sample line, an alternative is to use the CVCS letdown line as the source of the corrosion product sample. It has been argued that a CVCS letdown sample is not representative of the distribution in RCS, but experience at Vandellòs II suggests that this is not correct. Due to Vandellòs II's successful methods, the basic simplicity of the CVCS sample panel, and the probability that a similar approach could be used in most PWRs, this report encourages all PWRs to evaluate using Vandellòs II's method.

EPRI Perspective

Significant system modifications to improve RCS hot or cold leg sampling methods are costly and may not be practicable for many existing plants. Although existing RCS practices may not be ideal for independently following and analyzing soluble versus particulate corrosion product transients, they may still be satisfactory for developing qualitative trends for total soluble plus particulate corrosion product concentrations. These practices also are useful in detecting and following abnormal particulate releases from the core. However, unless care is taken, results both soluble and particulate concentrations—may be biased high by factors between ten and onehundred. This work provides a comprehensive review and update of RCS sampling practices, which had last been updated in appendix F of Revision 5 of the *PWR Primary Water Chemistry Guidelines* (EPRI report 1002884).

Keywords

Primary chemistry Reactor coolant system Sampling Corrosion products

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CONTENTS

| 1 INTRODUCTION | 1-1 |
|--|-----|
| 2 BACKGROUND TO RCS SAMPLING TECHNOLOGY | 2-1 |
| 3 EXISTING SAMPLING PRACTICES | 3-1 |
| 3.1 Conventional Corrosion Product "Grab" Samples | 3-2 |
| 3.2 Evacuated Glass Bottle "Grab" Samples | 3-4 |
| 4 CONTINUOUS CORROSION PRODUCT SAMPLING | 4-1 |
| 4.1 Background | 4-1 |
| 4.2 Continuous Sampling and Analysis Methods | 4-3 |
| 4.2.1 Sizewell B | 4-3 |
| 4.2.2 Ringhals (4, 33) | 4-9 |
| <i>5</i> HIGH TEMPERATURE RCS HOT LEG CORROSION PRODUCT SAMPLING AT DIABLO CANYON AND CATAWBA | 5-1 |
| 6 CVCS LETDOWN LINE SAMPLING | 6-1 |
| 7 ANALYSIS METHODS | 7-1 |
| 8 CONCLUSIONS | 8-1 |
| 9 REFERENCES | 9-1 |

LIST OF FIGURES

| Figure 2-1 Changes in Soluble Nickel and Cobalt Concentrations at Doel 1 Due to Changes in Flow Rate | 2-5 |
|--|------|
| Figure 2-2 RCS Particulate Concentrations at Ringhals 2 Following Start-up After Refueling in 1995 (Red – 0.5 to 1.0 μ m, Blue – 1.0 to 5.0 μ m) | 2-5 |
| Figure 2-3 Change in RCS Particulate Concentrations at Ringhals 2 Due to a Power Reduction to 50% | 2-6 |
| Figure 2-4 Changes in Measured Particulate Concentrations at Ringhals 2 Due to Changes in Flow Rate a - All Sample Line Valves Closed and Opened, b - Flow Rate Changed From 250 to 350 litre h ⁻¹ , c - Flow Rate Changed From 350 to 250 litre h ⁻¹ , d - Flow Rate Changed From 250 to 100 litre h ⁻¹ , e - Flow Rate Changed From 100 to 250 litre h ⁻¹ , f - Cooler Flow Reduced – Outlet Temperature Increased From 45 to 65°C (113 to 149°F), g - Monthly Control Rod Movement | 2-6 |
| Figure 3-1 Cobalt-58 and Cobalt-60 Concentrations at Vandellòs II From Cycle 3 to Cycle 7 Measured Using Filtered RCS Hot Leg "Grab" Samples | 3-3 |
| Figure 3-2 Cobalt-58 and Cobalt-60 Concentrations at Sizewell B From Cycle 1 to Cycle 7 Measured Using Filtered RCS Hot Leg "Grab" Samples Collected in an Evacuated Glass Vessel | 3-5 |
| Figure 4-1 Sampling Arrangement at Penly 1 Using a Normal Sample Line Instead of a Capillary Line | 4-2 |
| Figure 4-2 Triple Take-off Capillary Sampler | 4-7 |
| Figure 4-3 Capillary Line Sampling Arrangement at Sizewell B | 4-8 |
| Figure 4-4 Schematic Arrangement of the Capillary Sample Lines Installed at Ringhals 2 PWR | 4-10 |
| Figure 4-5 Arrangement of One of the Capillary Sample Lines Installed at Ringhals 2 PWR | 4-11 |
| Figure 4-6 Total Iron (Blue), Total Nickel (Green) and Total Cobalt (Red) Concentrations at Ringhals 2 (Top), Ringhals 3 (Middle) and Ringhals 4 (Bottom) Over Four Fuel Cycles From 2001 to 2005 | 4-13 |
| Figure 4-7 Iron (Top), Nickel (Middle) and Cobalt (Lower) Concentrations at Ringhals 2. Soluble Data in Red, Particulate <0.45 μ m in Blue and Total in Green | 4-14 |
| Figure 4-8 Total Cobalt-58 (Top) and Cobalt-60 (Lower) Concentrations at Ringhals 2 Obtained by "Grab" Sampling | 4-15 |
| Figure 5-1 Diablo Canyon High Temperature Sampler | 5-3 |
| Figure 5-2 High Temperature Filter Schematic | 5-4 |
| Figure 5-3 High Temperature Filer Housing | 5-5 |
| Figure 6-1 Vandellòs II CVCS Sample Panel | 6-3 |

| Figure 6-2 Corrosion Product Radionuclide Concentrations at Vandellòs II Measured Using the CVCS Sample Panel. | 6-4 |
|---|-----|
| Figure 6-3 Elemental Corrosion Product Concentrations at Vandellòs II Measured Using | |
| the CVCS Sample Panel | 6-5 |

LIST OF TABLES

| Table 4-1 Corrosion Product Concentrations for Different Reactor Types | 4-5 |
|---|-----|
| Table 5-1 Soluble and Particulate Concentrations at Catawba 1 and Diablo Canyon 1 | 5-7 |
| Table 5-2 Corrosion Product Radionuclide at Catawba 1 | 5-8 |

1 INTRODUCTION

PWRs do not have a standard requirement to measure RCS corrosion product concentrations during normal operation, other than that associated with the Standard Technical Specifications for \overline{E} , the average disintegration energy. Instead, a variety of plant specific sampling practices have evolved, which are dependent on the manpower available and the staff's interest in sampling the RCS for corrosion product activity. In general, corrosion product measurements are given a low priority, but the growing problems associated with the formation of crud on the fuel means that greater emphasis needs to be placed on obtaining representative corrosion product measurements. These will then indicate the onset of plant problems, particularly those associated with increases in the particulate burden in the RCS. Timely detection of increased corrosion product concentrations will aid in the evaluation of any risks associated with the onset of an Axial Offset Anomaly (AOA), increased shutdown releases, increased out-of-core dose rates or increased personnel doses.

Significant system modifications to improve RCS hot or cold leg sampling methods are costly, and may not be practicable for many existing plants. Therefore, the purpose of this report is to provide an historical review of sampling technology literature to illustrate the potential caveats inherent in interpreting data obtained using many current systems. It then describes examples of normal "grab" sampling methods and alternative methods in use at some plants to give improved RCS data. Although existing RCS practices may not be ideal for independently following and analyzing soluble versus particulate corrosion product transients, they may still be mainly satisfactory for developing qualitative trends for total soluble plus particulate corrosion product concentrations and are useful in detecting and following abnormal particulate concentrations, may be biased high by factors of between ten and one hundred.

Instead of analyzing an RCS hot or cold leg sample, the CVCS letdown line can be used as the source of the corrosion product sample. This has the potential disadvantage that the lower temperature and flow rate in the letdown line might modify the distribution between soluble, colloidal and particulate species in the RCS, and that it might reduce the total particulate burden. However, it has the more important advantage that the interactions that occur between soluble species and the oxides present in the high temperature parts of the sample line are absent. At Vandellòs II it has been shown that very reliable corrosion product measurements can be obtained in practice using a CVCS sample that is similar to those obtained using the best RCS sampling methods. This method is also described in this report and it is anticipated that it may be capable of being used at many other PWRs to give an improved understanding of corrosion product behaviour in higher duty cores.

2 BACKGROUND TO RCS SAMPLING TECHNOLOGY

Two sample points are normally used for primary coolant corrosion product analysis in Westinghouse and CE PWRs. These are the RCS hot leg and the CVCS letdown line, although an RCS cold leg sample point may also be available in some plants. B&W PWRs use one of the RCS cold legs for the reactor coolant sample. The RCS hot leg (or B&W PWR cold leg) sample line usually, but not always, has a delay coil to provide a 60-second or longer delay to reduce nitrogen-16 activity and typically the sample line is up to 600 feet (~200 m) long. Commonly, the line is made from 3/8-inch (10 mm) stainless steel tubing and is routed through the containment wall to a central sample room located in the auxiliary building, where it is cooled to ambient temperature. Due to the length of the sample line, the coolant transit time from the RCS to the sample point can be 10 to 15 minutes, but this depends on the flow rate. Normally, two containment isolation valves are fitted to the RCS sample line. At many U.S. PWRs these double containment isolation valves must be opened each time an RCS sample is collected, but in a number of European plants these valves normally remain open and there is a continuous sample line flow to a boronmeter and/or the volume control tank (VCT). In addition to the containment isolation valves, there are normally other isolation valves, drain lines and vent connections in the sample line, all of which can act as crud traps affecting measured particulate concentrations, as well as changes in tube diameter. Examples of the valves and other connections included in an RCS hot leg sample line are shown in the figures included in this report for RCS sampling at Sizewell B and Penly 1, although exact details will vary from plant to plant. In U.S. PWRs a purge flow to the VCT lasting for only 10 to 15 minutes at 0.1 to 0.5 gpm $(0.4 \text{ to } 2 \text{ litre min}^{-1})$ is often used to flush the sample line. Limitations on the number of operating cycles for the hot leg isolation valves has prompted some US plant operators to limit the use of hot leg RCS sample lines. At these plants the CVCS letdown lines are the only alternative for collecting primary coolant samples. After purging the sample line, a local sampling valve is opened and a cooled sample is collected for analysis.

The CVCS letdown line normally operates at a flow rate of 45 to 120 gpm and is taken from one of the RCS cold legs. It is cooled to approximately 290°F (143°C) as it passes through the shell side of the CVCS regenerative heat exchanger and the pressure is reduced 300 to 350 psig by pressure reducing valves or orifice plates, which also control the letdown flow rate. The CVCS letdown flow is then cooled to approximately 115°F (46°C) by the letdown heat exchanger, before the flow is routed either to the CVCS demineralizers or directly to the VCT. Typically, a CVCS sample line is about 175 feet long. One concern when using a CVCS letdown line sample is that particulate deposition can occur during the pressure reductions step and that the solubility changes occur as the letdown stream cools, since corrosion products are more soluble in the cooled CVCS letdown the length of a RCS sample line, so that the measured soluble concentrations from both the RCS and CVCS sample lines may be comparable.

As stated above, PWR sampling systems were not designed to obtain representative samples of trace corrosion products species. Instead the design criterion was to deliver a representative liquid sample for soluble boron and soluble fission product analysis without exposing the operator to excessive radiation. The sample lines installed are long, small-bore tubing and have an uneven temperature gradient over their length. When used to measure corrosion products, particle interactions occur with the sample line walls and crud traps and there are changes in corrosion product solubility. The latter are the result of the change in acidity of the primary coolant as the sample cools and the increase in solubility due to cooling. Unless care is taken, these changes will prevent the collection of samples that are sufficiently representative of the actual coolant state to enable quantitative interpretation of changes in particulate and soluble chemistry and transport from the core/plant surfaces to be made (<u>1</u>).

Modeling of sample systems show that deposited particulate on sample lines build up to a steady-state value quickly at high velocities, but slowly at low velocities. Approximately one month is required for equilibrium to be established for 5-micron particles transported at 121°C (250°F) in 0.65-inch ID tubing (2). A 15-minute sample line purge, therefore, does not establish equilibrium, nor does using a criterion to flush the line for three sample line volumes at typical sample line flow rates. The minimum deposit weight of 5-micron particles on a 0.65 inch ID sample line at 121°C is predicted to occur at approximately 6 ft s⁻¹ linear flow. However, the linear flow rate through 3/8-inch OD tubing having a nominal inside diameter of 0.245 inch is only 0.88 ft s⁻¹ at 0.13 gpm and 3.4 ft s⁻¹ at 0.5 gpm (common purge rates), rather than 6 ft s⁻¹. The latter would require a flow rate of 0.89 gpm for 3/8-inch tubing. The deposit mass continually increases as the particle diameter increases from 0.1 to ~1 micron, at which time the deposited mass stabilizes.

Although the RCS contains a mixture of soluble, colloidal and particulate species, it has become conventional to split these into two main fractions. These are a "soluble" fraction, which will pass through a 0.45 μ m Millipore or similar filter paper, and a "particulate" or "insoluble" fraction, which is retained on a 0.45 μ m filter. The "soluble" fraction will always contain a mixture of the true soluble fraction, any colloids and all small particulate species. Under some circumstances other micron cut-off sizes can be used, but the 0.45 μ m cut-off is the most common size used. As larger particles have a higher mass, they may produce a high mass fraction, even though a greater number of particles may be of much smaller size. Although it has suggested that a significant fraction of the corrosion products in the RCS are present as colloidal species, no definitive evidence for this exists and it would be expected that ferrous iron, the dominant corrosion product, will be present as a soluble species under the strongly reducing conditions that exist in the RCS. This will not be the case as soon as the coolant is exposed to air, when colloidal ferric hydroxide will form and other corrosion product radionuclides will coprecipitate. Colloidal species are a known problem under aerated conditions, particularly when analysing various PWR liquid radwaste streams.

To ensure that the particle concentration in the sample is representative, ASTM D 3370-95a, *Standard Practices for Sampling Water from Closed Conduits*, recommends sample line stability in addition to linear flow rate considerations. Experience with an RCS hot leg capillary sample line at Sizewell B (<u>3</u>) and the Ringhals PWRs (<u>4</u>) confirms the ASTM concern for flow stability. At Sizewell B the sample flow is stabilized for approximately two weeks prior to a sampling campaign, and at both Sizewell B and Ringhals any disturbance (e.g., valve manipulations) invalidates the results for several days. Maintaining a continuous, constant flow in the sample

line also avoids particulate and soluble transients associated with the movement of the temperature front along the sample line. At Sizewell B the hot leg sample stream flows to a gross gamma monitor and a boronmeter, which flow continually at about 900 ml min⁻¹ to the VCT, and three capillary streams from the hot leg each flow continuously at 84 ml min⁻¹. At Ringhals there is a bypass flow to the VCT with a flow rate of 200 kg h⁻¹. Isokinetic sampling is preferred because of varying sizes and densities of particles in a flowing stream. However, in plants with low particulate concentrations satisfactory results can be obtained with non-isokinetic sampling. The UKAEA preference is to place the capillary head immediately after a sample cooler, but at Sizewell B each capillary line is installed immediately in front of the cooler and is cooled individually. Sizewell B and Ringhals experience indicates that particulates are of lesser importance, except during transients, since they amount to only a fraction of the total corrosion product burden in the RCS. RCS particulate is mainly (<95%) 1 micron or less in diameter and are readily collected by the sample lines, thus isokinetic sampling is of less importance in the Sizewell B work. However, this may not always be true if large amounts of particulate are present in the primary coolant, e.g., plants suffering from AOA or those producing large particulate shutdown releases.

In addition to sample delivery considerations, a concern is that colloidal and particulate corrosion products will dissolve as the sample stream flows through the sample line. This is due to the drop in temperature along the sample line and the change in pH that occurs, both of which increase corrosion product solubility. A much more serious concern is that exposure to oxygen in the air will cause corrosion products to precipitate (5). The former occurs because the cooled sample line stream is less basic, or more acidic if lithium concentrations are low, due to the increased overall boric acid ionization that occurs as the temperature falls, and because corrosion product solubility is highest at an intermediate sample line temperature. Under the reducing conditions that exist in the RCS, iron and nickel solubility increases as the temperature falls along the length of the sample line, reaching a maximum value at about 150°C. These changes will increase soluble concentrations by dissolving colloidal species, or by partial or complete dissolution of larger particulate.

Oxygen has two possible effects. The first is that the nickel solubility might increase significantly, but the rate of dissolution may be too slow in the absence of the core radiation field for this to be a detectable effect. The second effect, and a serious problem, is that the dominant RCS species present is elemental ferrous iron, which will oxidize to ferric iron when a sample is exposed to air. When this occurs, the iron will precipitate out as sparingly soluble iron (III) hydroxide, or hydrated iron (III) oxide. Iron (III) hydroxide is commonly used as a scavenger in radiochemical analyses to remove trace radionuclides and even in slightly acidic solutions iron (III) forms insoluble hydroxides. The consequence is that other soluble corrosion product radionuclides co-precipitate with the excess elemental iron, including chromium-51, cobalt-58, cobalt-60, iron-59, manganese-54, as do fission products, such as cesium-134 and cesium-137. Thus, local grab samples, including both RCS and CVCS letdown samples, will give misleading information on the distribution between particulate and soluble species if the sample is filtered in the laboratory. However, the total concentration of soluble plus insoluble corrosion products might qualitatively trend with observed changes in activity transport, although the result may still be biased high.

In work reported by Bridle ($\underline{6}$) a continually flowing capillary steam approximating to isokinetic sampling from the RCS hot leg was used with an approximately 112 seconds transit time. Particulate was collected on a 0.1-micron Millipore or Nuclepore polycarbonate membrane filter followed by two Acropor cation membranes and two anion membranes in the same sample holder. Noe et al. ($\underline{7}$) showed that the difference between soluble and particulate cobalt-58 and cobalt-60 were related to the sample line history. At high boron at beginning of a fuel cycle, cobalt activity from previous operations dissolved during delivery in the sample line, resulting in a decrease in the soluble cobalt-58 to cobalt-60 activity ratio. This suggests that RCS hot sampling is preferred over samples that are conditioned, however experience at Vandellòs II indicates that CVCS sampling can also be used successfully in practice (see below). However, Bridle et al. ($\underline{8}$) reported that soluble transition metal ions interact with the hot sample line. The pH of the cooled sample is sensitive to the boron/lithium ratio during the cycle, and at end of core life significant pH increases occur in the conditioned sample.

Due to the way that corrosion products interact with the oxides deposited within the sample line and the way that the temperature along an RCS sample line will change with flow rate, altering the sample line flow rate can be expected to affect the measured soluble corrosion product concentration. Polley and Brookes (9, 10) reported that increasing the sample flow rate from 25 g s⁻¹ to 100 to 125 g s⁻¹ at Ringhals 3 caused a decrease in soluble cobalt-58 and cobalt-60 concentrations by a factor of up to 100 times. A more detailed study of the effect of flow rate changes was carried out at Doel 1 (<u>11</u>), as shown in Figure 2-1, which is discussed more fully in Section 3.1. Elemental concentrations for the DIDO Water Reactor at Harwell were shown to vary inversely with sample flow rate, particularly for sample lines with long residence times. In addition to soluble transients, particulate transients lasting for up to one week also occur from sample line valve operation, as well as from primary circuit operations such as changing power or the routine test movement of the control rods. Examples of these types of effects at Ringhals 2 are shown in Figures 2-2 to 2-4 (<u>4</u>, <u>12</u>).

As is evident from Figures 2-1 to 2-4 disturbances in the sample line flow rate, including initially opening the line, causes transient soluble and particulate corrosion product peaks, which will give a result that can be biased high by ten to one hundred times. If a continuous sample line flow cannot be used, such effects are best avoided by using a prolonged high flow rate purge, such as that used at Ringhals 3 or Vandellòs II (Section 3.1). It is also evident that using the same flow rate and purge time is essential if reproducible results are to be obtained.

Roesmer reported studies (<u>13</u>, <u>14</u>) that suggested that "hot" samples are more indicative of actual crud conditions in the circulating reactor coolant since solubility increases as the temperature falls. An important consideration in Roesmer's work was the relationship between the volume of sample filtered and the deposit on the inline crud filter; large sample volumes resulted in significant dissolution of crud collected on the inline filter. Dissolution of the crud was particularly important for samples that were conditioned. Roesmer concluded that the ratio of "hot" to ambient crud should be between 2.4 and 5.3 if no dissolution from the filter matrix were to take place.



Figure 2-1 Changes in Soluble Nickel and Cobalt Concentrations at Doel 1 Due to Changes in Flow Rate





RCS Particulate Concentrations at Ringhals 2 Following Start-up After Refueling in 1995 (Red – 0.5 to 1.0 μ m, Blue – 1.0 to 5.0 μ m)



Figure 2-3 Change in RCS Particulate Concentrations at Ringhals 2 Due to a Power Reduction to 50%



Figure 2-4

Changes in Measured Particulate Concentrations at Ringhals 2 Due to Changes in Flow Rate a - All Sample Line Valves Closed and Opened, b - Flow Rate Changed From 250 to 350 litre h⁻¹, c - Flow Rate Changed From 350 to 250 litre h⁻¹, d - Flow Rate Changed From 250 to 100 litre h⁻¹, e - Flow Rate Changed From 100 to 250 litre h⁻¹, f - Cooler Flow Reduced – Outlet Temperature Increased From 45 to 65°C (113 to 149°F), g - Monthly Control Rod Movement.

3 EXISTING SAMPLING PRACTICES

As described in Section 2.0, existing sampling systems in most PWRs will not deliver representative samples of distinct particulate vs. colloidal vs. dissolved corrosion products. Most sampling practices only "sample the sample line," but nevertheless these will show abnormal releases, particularly of particulate, from the core/plant surfaces. Redesigning existing reactor coolant sampling systems to provide adequate sample delivery that considers flow kinetics (e.g., Sizewell B and Ringhals sample systems – see Section 4) is not feasible for most PWRs. At least one U.S. plant has adopted a compromise practice of collecting samples at 64°C (147°F) with a steady flow through the existing sampling system (<u>15</u>). A major consideration in obtaining reliable RCS corrosion product samples is the need to provide a continually flowing system without flow disturbances and without exposure to air/oxygen. Sizewell B, for example, allows about two weeks for sample line transients to disappear, while Ringhals does not permit any sample line valve movements during integrated sample collection. However, an acceptable alternative source of an RCS sample may be to use a CVCS sample collected in an in-line filter holder, as used successfully at Vandellòs II – see Section 6.

Flow changes cause transients in the soluble concentrations and hence changes in the final equilibrium concentrations within the sample line, the latter being inversely proportional to the sample line flow rate. UKAEA (<u>11</u>) attributed these effects to changes in the interaction of soluble corrosion products with the oxides on the sample line surface, as a result of changes in the temperature profile along the sample line with changes in flow rate. Additional studies carried out by UKAEA indicate that deposition of cobalt onto the sample line surfaces is mass transfer controlled at 300°C (572°F) and 210°C (410°F), and kinetically controlled at lower temperatures (<120°C (248°F)). Due to these interactions, what is measured may not be identical to the concentrations in the RCS in an absolute sense, but it should be of significance in a relative sense. The key factors for obtaining reasonably accurate corrosion product analyses in the circulating reactor coolant can be summarized as:

- 1. purging the RCS hot leg sample line adequately,
- 2. using a consistent, and preferably high sample line flow rate and
- 3. avoiding exposure to air if soluble and particulate fractions are required.

Due to the limitations on isolation valve use in U.S. PWRs, each plant should evaluate its local sampling limitations to determine how these might impact interpretation of sampling data. However, under suitable conditions, purging a sample line for only 30 minutes may still provide reproducible results for trending purposes that are nevertheless quantitatively biased.

Existing Sampling Practices

The following two examples illustrate the different results that can be obtained using two different "grab" sampling methods. These give data for Sizewell B and Vandellòs II, from which comparisons can be made with data obtained using a continuously flowing RCS capillary samplers (Section 4) and a CVCS sample panel (Section 6), respectively.

3.1 Conventional Corrosion Product "Grab" Samples

As has been described above, the normal method of corrosion product sampling is to purge the RCS sample line for up to 30 minutes and then to collect an RCS sample in an open plastic bottle or a sample bomb. If any separation is carried out, it will often be done in the laboratory some time after the sample has been collected. This approach was used at Vandellòs II until its CVCS sample panel was commissioned in Cycle 8 (<u>16</u>). It is still used (without filtering) during shutdown and start-up to give total corrosion product concentrations when the concentrations are high enough to saturate the cation filter used in the CVCS sample panel. A notable feature of the RCS sample method is the use of a higher flow rate purge for one hour than is used in most PWRs, which minimized the bias in the earlier results. The results obtained at Vandellòs II are given here as an example of what can be expected from a normal type of "grab" sample method, and for comparison with the results obtained using its CVCS sample panel.

At Vandellòs II the RCS hot leg sample line was, and still is, purged for one hour at 1300 ml min⁻¹ to the VCT. A 250 ml sample is then collected for radiochemical analysis in an open plastic bottle (<u>16</u>). Up to Cycle 7 the sample was filtered through a 0.45 μ m Millipore filter in the laboratory to give "so-called" soluble and insoluble radionuclide fractions. Examples of the results obtained are shown in Figure 3-1, which give cobalt-58 and cobalt-60 data for Cycles 3 to 7.





For cobalt-58, cobalt-60 and other corrosion product radionuclides, the characteristic measured soluble/insoluble distribution was that the insoluble fractions were always much higher than the soluble fractions. For cobalt-58, there was apparently over one hundred times more particulate than soluble species in the RCS coolant (Figure 3-1), while for cobalt-60 there was apparently over ten times more particulate. The other characteristic was a relatively high scatter in the data and the "boat"-shaped concentration changes during the cycle. Another feature was that there was apparently more insoluble manganese-54 than soluble manganese-54, and that some cesium-134 and cesium-137 was always present in the insoluble fraction; all these nuclides should only appear in the soluble fraction. Although only a limited number of equivalent CVCS samples were analyzed, these gave similar results when filtered in the laboratory.

These results are similar to those often reported at other PWRs, although many PWRs do not filter the samples.

3.2 Evacuated Glass Bottle "Grab" Samples

As the main problem when attempting to measure RCS particulate and soluble corrosion product fractions is precipitation of soluble elemental ferrous iron when the sample is exposed to air, an improvement is to collect the sample in an evacuated sample vessel and to filter it under inert conditions. A method based on this principle was developed at Ringhals, and is used as the standard method at Sizewell B. A similar method is used at Philippsburg 2.

As used at Sizewell B (17), the sample is collected in a 200 ml glass vessel, which has taps at each end and a rubber septum on the side of the upper part of the vessel. Before collecting a sample the vessel is evacuated for 15 minutes, flushed with argon and evacuated again for 30 minutes. Concurrently, a flexible hose fitted with a "quick-disconnect" fitting at one end and a needle at the other is connected to the RCS sample line, which is flushed for 20 minutes at 5 litre \min^{-1} at a back pressure of 2 bar. At Sizewell B the main sample line also flows to a boronmeter and only a short section needs to be flushed (see Figure 4-3). To collect a sample, the needle is inserted through the septum and a 100 ml sample is collected, half filling the vessel. After sampling, the vacuum is released using argon and, if required, a 15 ml gas sample taken from the gas space for noble gas or hydrogen analysis. The liquid phase is filtered through a filter stack, consisting of combinations of (1) a 0.45 μ m Millipore filters (top), (2) up to three 0.45 μ m Gelman anion filters, (3) a further 0.45 μ m Millipore filter and (4) up to three 0.45 μ m Gelman cation filters (bottom), although not all may be used. Filtration is carried out under an argon purge, although complete oxygen exclusion is difficult. The separated filters are counted to give an insoluble fraction (1), an anion fraction (2 + 3) and a cation fraction (4). Results obtained using this method during Cycles 1 to 7 are shown in Figure 3-2, which may be compared with the results obtained using a capillary sample line given in Table 4-1.

Compared with the "grab" results from Vandellòs II, this method gives similar soluble and insoluble radiocobalt concentrations, which are similar to those observed using the capillary sample line (Table 4-1). However, compared with the data in Table 4-1, and as shown in Figure 3-2, the "grab" sample data tend to be biased high and there are considerable scatter in the data (especially for the insoluble fraction). In addition, the insoluble concentrations are normally higher than the soluble concentrations, whereas the reverse is true for data obtained using a capillary sample line. Even though the results are biased and the scatter is higher than ideal, both of which must be due to the flow rate changes when purging the line, the "Ringhals" method produced acceptable routine data up to Cycle 5.



Figure 3-2 Cobalt-58 and Cobalt-60 Concentrations at Sizewell B From Cycle 1 to Cycle 7 Measured Using Filtered RCS Hot Leg "Grab" Samples Collected in an Evacuated Glass Vessel

In Cycles 6 and 7 problems developed due to a combination of the lower RCS cobalt-58 concentrations at Sizewell B and the presence of cesium-134 and cesium-137 in the coolant, which raised the minimum detectable activity. To overcome this problem a new method is being evaluated (<u>17</u>) in which a 47 mm pressure-rated Millipore filter holder is connected to one of the capillary sample lines and the particulate fraction from about 100 litre of primary coolant is collected over 24 hours on a 0.45 μ m Millipore filter. The soluble fraction is obtained by passing the final 400 ml of sample through a filter stack (three 0.45 μ m Gelman cation filters (top), a 0.45 μ m Millipore filter and three 0.45 μ m Gelman anion filters (bottom)). This method is similar to that now used at Ringhals, and minimizes particulate transient effects and improves detection limits because of the greater amounts filtered. As the particulate fraction has already been removed, the filter stack does not need to be protected from exposure to the air.

4 CONTINUOUS CORROSION PRODUCT SAMPLING

4.1 Background

As described in Section 3, the primary coolant contains a mixture of soluble, colloidal and particulate species that are normally separated into filterable and non-filterable fractions by filtration through a 0.45 μ m filter. The non-filterable fraction contains soluble, small particulate and colloidal species and the filterable fraction larger particulate species, but, as described above, the relative concentrations are modified by solubility changes that occur in the sample line during sampling.

Above about 200°C (392° F) (<u>11</u>), soluble corrosion product RCS sampling is affected by mass transfer controlled multiple deposition and re-release steps in the high temperature sections of the sample lines, which affects transport of elemental and radioactive corrosion products for periods of a few days or longer. When sample line flow rates are changed, these deposition/re-release effects produce transient changes in both soluble and particulate concentrations over periods also lasting for hours or days. At both Doel 1 and Ringhals 3 (<u>9</u>, <u>10</u> and <u>11</u>), it was shown that transient concentration peaks were produced and that the "apparent" equilibrium soluble concentrations measured after these transients had passed were different for different flow rates, and were lower at higher sample line flow rates (see Figure 2-1). At lower temperature, deposition and re-release becomes kinetically controlled and slow, and sample line effects disappear. The latter, together with the much higher soluble concentrations, is the reason why good results can usually be obtained at shutdown and startup.

Particulate sampling and particle size measurements are also influenced by changes in sample line flow rate, particularly that associated with the initial opening of sample line valves. These changes cause particulate re-suspension from multiple dead legs existing in all sample lines (isolation valves, drain lines, "tee"-pieces, changes in tube diameter, etc.). The transient peaks can last for hours or sometimes days. Examples of such effects at Doel 1 and Ringhals 2 obtained using capillary samplers are shown in Figures 2-1 to 2-4 (<u>4</u>, <u>10</u> and <u>11</u>). Similar effects are seen at Sizewell B.

Due to the problems associated with corrosion product sampling, most measured soluble and particulate concentrations obtained by conventional sampling and analytical techniques are not reliable ($\underline{12}$ to $\underline{21}$). For example, measured ratios of soluble to particulate concentrations for normal bottle samples can range from ~0.05 at the VVER stations Paks and Loviisa, to ~0.1 in many US PWRs, and ~1.0 in Siemens PWRs, whereas they are ~10 in Westinghouse PWRs using sample line filters (e.g. Sizewell B, Ringhals and Vandellòs II). Except for possibly the recent measurements made on AOA affected stations (where the RCS nickel concentration has been reported to exceed nickel or nickel oxide solubility), high particulate fractions are almost

Continuous Corrosion Product Sampling

certainly due to redox changes after sampling causing precipitation of iron hydroxide and scavenging of other radionuclides from the samples. It is believed that systems that sample from cold coolant systems (as in VVER-440 stations where RCS samples are taken from the cooled coolant purification loops at 50 to 60°C (122 to 140°F)) or where the sample lines are cooled locally (as in later Siemens PWRs) give more reliable results for the process line concentrations than conventional sampling from the RCS when high temperatures exist up to the sample room, but only if the soluble and particulate fractions are separated before being exposed to air.

From the discussion above, the essential requirement in obtaining reliable RCS hot or cold leg corrosion product samples is to use a continuously flowing sample line and to avoid any changes in flow rate. Operation of any sample line valves must be avoided. Ideally, the sample line should operate at a relatively high flow rate and should sample particulates at an isokinetic flow rate, so that particulates are sampled representatively. However, in practice inertially depositing particulate concentrations are so low that isokinetic sampling is not normally necessary. Furthermore, if the capillary sampler is fitted so that it re-samples a normal sample line (or indeed any other sampling device, e.g. a particulate sampler), it must be recognized that the initial sampling from the RCS will not be isokinetic. If a capillary line is used semi-continuously it needs to be allowed to flow for at least 1-2 weeks before reliable samples can be taken to avoid flow rate change effects, and further changes in flow must be avoided.

Penly Sampling Arrangement





In most cases, UK workers have used capillary sample lines that re-sample the RCS hot leg sample line, and this approach is used at Sizewell B and Ringhals 2 to 4 (<u>15</u>). However, a capillary line is not an absolute essential and, for example, results which were almost as satisfactory were obtained at the EDF PWR Penly 1 using a ~10 mm I.D. line "teed"-off a continuously flowing hot leg sample line to the RCS boronmeter (Figure 4-1).

Irrespective of the specific sample system design, ideally the sample stream must be filtered before it leaves the sample line (to avoid changes due to iron (III) hydroxide precipitation) and then passed to an analytical system that either directly analyses the coolant or collects the elemental transition metals and radionuclides in an integrated sampler for later on-site or off-site analysis.

Continuous capillary line sampling with *in situ* filtration at the capillary line outlet, normally followed by immediate transition metal ion chromatography analysis for Fe, Ni, Co, Mn, Zn and Cu, is used at Sizewell B as a research tool and has been used by UK workers to make comparative measurements at a number of PWRs and VVERs (Table 4-1, <u>22</u> to <u>28</u>). Alternatively, at Ringhals, the sample can be passed through a filter stack arrangement (a Millipore filter, plus a two cation ion-exchange membranes), to produce a stable integrated sample that reduces interferences, reduces scatter and lowers detection limits. A similar approach was used at Loviisa, where an ion chromatograph concentrator column was used to collect soluble corrosion products followed by ICPMS (inductively coupled plasma mass spectrometry) and -spectrometry analysis of the eluted corrosion products (<u>26</u> and <u>27</u>).

It must be stressed again that the samples obtained in this way still do not necessarily represent the soluble and particulate concentrations that exist in the RCS itself, since colloid dissolution or particulate precipitation still occurs in the sample line as it cools and its pH changes. However, the samples will be reproducible from sample to sample and will be free of transient effects caused by opening the sample system valves. Even when analyzed in this way, it is apparent from Table 4-1 that continuous samples can still give appreciable variability in the results, particularly if the samples become contaminated with oxygen. The latter was the reason for the very low iron concentrations measured at Paks 1 and 2, which was due to the lack of inert gas stripping to degas the sample stream resulting in heavy iron plate-out on the walls of the sample stripper. In Table 4-1 the low iron results at Grohnde and Loviisa 2 were because "grab" sampling had to be used.

4.2 Continuous Sampling and Analysis Methods

4.2.1 Sizewell B

The sampling arrangement used at Sizewell B (29 to 32) is shown in Figures 4-2 and 4-3.

At Sizewell B an AEA Technology designed triple take-off stainless steel capillary sampler is installed in one of the two RCS hot leg sample lines. It is located in the normal auxiliary building nuclear sample room, immediately upstream of the main sample line cooler at a point where the sample line temperature is of the order of 250-270°C (482-518°F). Upstream, this sample flows past six isolation valves (including the two containment isolation valves), a non-

Continuous Corrosion Product Sampling

return valve, several changes in tube diameter and five side-arms, all of which can act as crud traps. Downstream, after cooling, the sample line feeds a boronometer, normally operated continuously at 66 kg h^{-1} , and is then returned to the volume control tank. It also supplies the normal grab sampling cabinet.

Three short thick wall stainless steel capillary lines (3.18 mm O.D. 0.74 mm I.D.) run from the capillary head to individual capillary line coolers and then run to automatic minimum dead volume isolation valves (which operate together with the containment isolation valves on a safety injection signal) and to coils of capillary tubing, which terminate in a sampling cabinet. Each line is provided with a manual shut-off valve in the cabinet. At Sizewell B the tubing in the sample line coolers and all the downstream tubing is made from 0.81 mm O.D. 0.51 mm I.D. stainless steel capillary line. Overall, each line contains 52 meters of capillary tubing, of which 12 meters are in the sample cooler. At 84 ml/min the linear fluid velocity through the capillary line is 6.85 m/s.

A drawing of the type of capillary sampling head used at Sizewell B is shown in Figure 4-2. This particular example was installed at Loviisa and differs in that Swagelok fittings were used; at Sizewell B all connections were welded to meet nuclear and seismic requirements. The Loviisa arrangement also differs in that no sample cooler was fitted, since at VVERs the sample is taken from the cooled coolant purification system operating at 55-60°C. At Sizewell B this arrangement is used for a second head fitted to the CVCS letdown line and could have been used if the RCS hot leg capillary head had been fitted downstream of the main sample line cooler. The latter approach is used at Ringhals, although here three individual single capillary sample heads are fitted.

When commissioned in 1994 for Hot Functional Tests, the measured flow rates of all three lines were 84-85 ml min⁻¹ at 155 bar g, reducing to 20 ml min⁻¹ at 24 bar g during the shutdown. No change in flow rate has occurred over eleven years of effectively continuous operation except temporarily at the start of each shutdown and startup, when significant particulate transients were caused by inserting the control rods or main coolant pump startup, respectively. However, these transient changes typically only last for a few hours. Such good performance is expected, since not only is the RCS particulate burden low but the maximum particle size is normally <1 μ m. This contrasts with the common experience with steam/water circuit capillary lines, which block easily due to the presence of larger size particulate iron oxides.

| Table 4-1 | |
|--|--|
| Corrosion Product Concentrations for Different Reactor Types | |

| | | | | Elei | mental Co | ncentratio | ns | | Radionuclid | Soluble | Specific | | |
|----------------------|-------|---------|---------------------|-------|----------------|------------|--------|--------|-------------|------------------------|----------|---------------------|---------------------|
| Diant | Cuala | Boron | | Cob | alt | Nic | kel | 60 | Со | 5 | °Co | Activ | vities |
| Plant | Cycle | mg kg⁻¹ | рп _{300°с} | (ng k | (g ⁻¹) | (ng | kg⁻¹) | (MB | iq m³) | (MBq m [·] ³) | | ⁶⁰ Co/Co | ⁵⁸ Co/Ni |
| | | | | sol. | insol. | sol. | insol. | sol. | Insol. | sol. | Insol. | (GBq g⁻¹) | (GBq g⁻¹) |
| Doel 1 | 16 | 480 | 7.00 | 6.5 | 0.4 | 680 | 750 | 0.09 | 0.10 | 21 | 25 | 14 | 31 |
| Doel 2 | 13 | 670 | 6.90 | 8.8 | - | 390 | - | 0.125 | 0.088 | 1.30 | 0.073 | 14 | 3.3 |
| Doel 4 | 1 | 230 | 7.40 | 10.0 | 2.30 | 78 | 33 | 0.027 | 0.044 | 0.39 | 0.41 | 3 | 5.0 |
| Doel 4 | 3 | 850 | 7.30 | 7.0 | - | 560 | - | 0.142 | 0.36 | 0.48 | 2.42 | 20 | 0.9 |
| Vandellòs II (a)(g) | 8 | 410 | 7.20 | 4.0 | <1 | 114 | 101 | 2.19 | 0.33 | 9.1 | 3.01 | 548 | 80 |
| Penly 1 (g) (b) | 4 | 375 | 7.00 | 6.4 | 0.49 | 138 | 56 | 0.97 | 0.039 | 5.46 | 0.71 | 146 | 39 |
| Ringhals 2 (d) | 17 | 400 | 7.21 | 3.5 | 0.5 | 67 | 19 | 0.202 | 0.045 | 0.26 | 0.15 | 73 | 4.4 |
| Sizewell B (b)(d)(e) | 1 | 535 | 7.25 | 4.2 | 0.38 | 134 | 48 | 0.0305 | 0.0202 | 0.49 | 0.278 | 7.1 | 3.5 |
| Sizewell B (b)(d)(f) | 1 | 152 | 7.34 | 4.0 | - | 111 | - | 0.0135 | - | 0.773 | - | 2.8 | 5.8 |
| Sizewell B (b)(d)(e) | 2 | 651 | 7.19 | 3.7 | 0.6 | 255 | 129 | 0.0308 | 0.0406 | 0.357 | 0.863 | 7.1 | 0.9 |
| Sizewell B (b)(d)(f) | 2 | 89 | 7.39 | 2.0 | - | 95 | - | 0.021 | - | 0.342 | - | 13.5 | 3.7 |
| Sizewell B (b)(d)(e) | 3 | 529 | 7.26 | 2.4 | 0.16 | 416 | 71 | 0.0489 | 0.0388 | 2.10 | 1.42 | 21.7 | 4.9 |
| Sizewell B (b)(d)(f) | 3 | 6 | 7.39 | 1.2 | - | 108 | - | 0.0197 | - | 1.02 | - | 15.7 | 11.0 |
| Sizewell B (b)(d)(g) | 4 | 1100 | 6.98 | 4.6 | 0.23 | 1161 | 64 | 0.116 | 0.0481 | 1.31 | 0.674 | 26.4 | 1.2 |
| Neckarwestheim 1 (j) | 13 | 450 | 7.30 | 9.1 | - | 80 | - | 0.728 | - | 1.43 | - | 82 | 2 |
| Neckarwestheim 1 (j) | 17 | 800 | 7.08 | 8.9 | - | 49.6 | - | 0.476 | 0.15 | 0.29 | 0.27 | 61 | 6 |
| Grohnde (i) | 4 | 380 | 7.40 | 7.9 | - | 38.8 | - | 1.67 | 0.87 | 2.07 | 2.1 | 214 | 53 |
| Trillo (j) | 7 | 280 | 7.42 | 5.0 | 0.77 | 20 | 22 | 0.14 | 0.041 | 0.044 | 0.46 | 29 | 2.1 |
| Philippsburg 2 (j) | 4 | 400 | 7.30 | 2.4 | 0.14 | 36.6 | 31 | 0.148 | 0.02 | 1.24 | 0.58 | 62 | 38 |
| Brokdorf (j) | 6 | 375 | 7.00 | 1.2 | - | 38.3 | - | 0.300 | 0.41 | 3.01 | 6.2 | 322 | 82 |
| Neckarwestheim 2 (j) | 1 | 440 | 7.30 | 1.7 | 0.20 | 14.1 | 26 | 0.058 | 0.0049 | 1.43 | 0.080 | 42 | 125 |
| Neckarwestheim 2 (j) | 5 | 700 | 7.13 | 2.2 | 1.8 | 83 | 99 | 0.23 | 0.29 | 0.82 | 0.46 | 114 | 13 |
| Loviisa 1 | 13 | 600 | 7.12 | 1.0 | 0.13 | 65 | 13 | 0.0059 | 0.0011 | 0.020 | 0.031 | 6 | 0.26 |
| Loviisa 1 (c)(j) | 16 | 144 | 7.27 | 0.9 | 0.7 | 13 | 29 | - | 0.0032 | - | 0.0077 | - | - |
| Loviisa 2 (i) | 10 | 580 | 7.15 | 2.1 | 0.05 | 57 | 8.3 | 0.011 | 0.003 | 0.010 | 0.009 | 20 | 0.28 |
| Loviisa 2 (c)(j) | 13 | 750 | 7.12 | 3.9 | 0.06 | 139 | 6.3 | 0.0094 | 0.003 | 0.013 | 0.0097 | 3.1 | 0.12 |
| Dukovany 3 | 7 | 350 | 7.15 | 1.3 | 0.04 | 85 | 8 | 0.047 | 0.002 | 0.091 | 0.016 | 35 | 1.07 |
| Paks 1 | 8 | 176 | 7.28 | 1.0 | 0.19 | 34 | 8.2 | 0.017 | 0.0013 | 0.011 | 0.0021 | 17 | 0.38 |
| Paks 1 (h) | 9 | 390 | 7.28 | 0.4 | <0.05 | 16.5 | <0.05 | 0.018 | 0.01 | 0.015 | 0.01 | 74 | 0.78 |
| Paks 2 (h) | 7 | 381 | 7.47 | 0.9 | 0.04 | 10.9 | 2.7 | 0.014 | 0.00096 | 0.008 | 0.0019 | 18 | 0.79 |
| Paks 2 (h) | 8 | 474 | 7.18 | 0.4 | <0.05 | 9.6 | <0.05 | 0.010 | 0.007 | 0.007 | 0.008 | 25 | 0.92 |

AEA Technology Ion Chromatography (IC) data, except

(a) Station in-line filter pack data (b) NE/BE/Magnox IC data (e) Mid-cycle

(f) End-of-cycle

(i) Grab samples

- (j) Continuous (non-capillary line) samples
- (c) VTT ICPMS data (g) Start-of-cycle

(d) Inconel 690 SGs

(h) Hydrazine Water Chemistry 1 MBq m⁻³ = $2.7 \times 10^5 \mu$ Ci ml⁻¹

Continuous Corrosion Product Sampling

Table 4-1 (continued)Corrosion Product Concentrations for Different Reactor Types

| | | Elemental Concentrations Radionuclide Activities | | | | | | | | | | Soluble | | | | | | | | | | | | | | | | | | | | | | | | | | |
|------------------|-------|--|-------------|------------|-------------------|----------|-----------------|-----------|----------------------------------|-------|----------------------------------|---------|----------------------------------|-------|--------------------|----------------------------------|---------------------|--|----------------------------------|--|----------------------------------|--|----------------------------------|--|---------------------|--|----------------------------------|--|---------------------|--|-------------------------------|--|-------------------------------|--|------------------------------|--|------------|------------------------|
| Plant | Cycle | lr (ng | on kg⁻¹) | Man (ng | ganese g kg⁻¹) | Z (ng | ′inc J kg⁻¹) | Co (ng | Copper (ng kg ⁻¹) | | Copper (ng kg ⁻¹) | | Copper (ng kg ⁻¹) | | Copper (ng kg¹) | | Copper (ng kg⁻¹) | | Copper (ng kg ⁻¹) | | Copper (ng kg ⁻¹) | | Copper (ng kg ⁻¹) | | Copper (ng kg⁻¹) | | Copper (ng kg ⁻¹) | | Copper (ng kg⁻¹) | | ^{₅₄} Mn (MBq m⁻³) | | ^{⁵⁰} Fe (MBq m⁻³) | | ^{⁵⁰} Fe (MBq m³) | | Cr qm³) | Specific Activities |
| | | sol. | insol | Sol | insol. | sol. | insol. | sol. | insol. | sol. | insol. | sol. | insol. | sol. | insol. | ^{₅₄} Mn/Fe (GBq g⁻¹) | | | | | | | | | | | | | | | | | | | | | | |
| Doel 2 | 13 | 1040 | - | 300 | - | - | - | - | - | 0.43 | 0.0017 | - | - | - | - | - | | | | | | | | | | | | | | | | | | | | | | |
| Doel 4 | 1 | - | 10 | 814 | 5.0 | - | - | - | - | 0.95 | 0.11 | 0.142 | 0.037 | ND | 1.08 | 0.41 | | | | | | | | | | | | | | | | | | | | | | |
| Doel 4 | 3 | - | - | 690 | - | - | - | - | - | 2.74 | 0.20 | 0.210 | - | - | - | - | | | | | | | | | | | | | | | | | | | | | | |
| Vandellòs II | 8 | 2150 | - | - | - | - | - | - | - | 2.88 | 0.077 | 0.534 | 0.0456 | ND | 2.31 | - | | | | | | | | | | | | | | | | | | | | | | |
| Penly 1 | 4 | 2320 | 101 | 167 | 2.6 | 288 | 6.6 | <2 | 2.2 | 3.9 | 0.0017 | 0.28 | 0.0013 | <0.18 | 0.65 | 1.34 | | | | | | | | | | | | | | | | | | | | | | |
| Ringhals 2 | 17 | 1710 | 1010 | 292 | 5.4 | 385 | 2 | 1.2 | 1.4 | 0.20 | 0.017 | 0.028 | 0.0069 | ND | 0.68 | 0.12 | | | | | | | | | | | | | | | | | | | | | | |
| Sizewell B | 1 | 5961 | 139 | 344 | 1.5 | 170 | 0.66 | 1.0 | 0.88 | 1.75 | 0.0172 | 0.151 | 0.0161 | ND | 0.547 | 0.29 | | | | | | | | | | | | | | | | | | | | | | |
| Sizewell B | 1 | 4496 | - | 551 | - | 382 | - | 21 | - | 2.51 | - | 0.0322 | - | ND | - | 0.54 | | | | | | | | | | | | | | | | | | | | | | |
| Sizewell B | 2 | 6123 | 322 | 157 | 3.4 | 126 | 15 | 10 | 4.8 | 2.32 | 0.0303 | 0.085 | 0.0177 | ND | 1.37 | 0.40 | | | | | | | | | | | | | | | | | | | | | | |
| Sizewell B | 2 | 3313 | - | 171 | - | 55 | - | 1.1 | - | 0.983 | - | 0.0322 | - | ND | - | 0.35 | | | | | | | | | | | | | | | | | | | | | | |
| Sizewell B | 3 | 4288 | 93 | 200 | 1.6 | 37 | <48 | 1.3 | 0.91 | 1.34 | 0.0276 | 0.0453 | 0.0235 | ND | 2.20 | 0.32 | | | | | | | | | | | | | | | | | | | | | | |
| Sizewell B | 3 | 202 | - | 91 | - | 13 | - | 0.82 | - | 0.443 | - | <0.009 | - | ND | - | 1.7 | | | | | | | | | | | | | | | | | | | | | | |
| Sizewell B | 4 | 7438 | 106 | 281 | 1.9 | 31 | <5.9 | 0.52 | <3.3 | 1.15 | 0.0279 | <0.13 | 0.0177 | ND | 2.17 | 0.165 | | | | | | | | | | | | | | | | | | | | | | |
| Neckarwestheim 1 | 13 | 498 | - | 75 | - | - | - | 2.2 | - | 0.485 | - | - | - | - | - | 0.97 | | | | | | | | | | | | | | | | | | | | | | |
| Neckarwestheim 1 | 17 | 1617 | - | 63 | - | 243 | - | 4.5 | - | 0.422 | 0.05 | 0.059 | - | ND | 2.04 | 0.26 | | | | | | | | | | | | | | | | | | | | | | |
| Grohnde | 4 | 265 | - | 63 | - | 274 | - | 15.5 | - | 1.07 | 3.3 | - | - | - | - | 4.04 | | | | | | | | | | | | | | | | | | | | | | |
| Trillo | 7 | 1465 | 52 | 68 | 0.75 | 39 | - | 2.4 | 0.52 | 0.36 | 0.014 | 0.11 | 0.012 | - | - | 0.25 | | | | | | | | | | | | | | | | | | | | | | |
| Philippsburg 2 | 4 | 3207 | - | 66 | - | - | - | - | - | 0.51 | - | 0.136 | - | - | - | 0.16 | | | | | | | | | | | | | | | | | | | | | | |
| Brokdorf | 6 | 1460 | - | 51 | - | 226 | - | 10.7 | - | 1.04 | 0.19 | 0.180 | 0.10 | ND | 0.22 | 0.71 | | | | | | | | | | | | | | | | | | | | | | |
| Neckarwestheim 2 | 1 | 972 | - | 148 | 2.5 | - | - | 5.2 | 1 | 0.907 | 0.0045 | 0.049 | 0.0056 | - | - | 0.93 | | | | | | | | | | | | | | | | | | | | | | |
| Neckarwestheim 2 | 5 | 2400 | 950 | 79 | 22 | 301 | 2 | 2.9 | 4 | 0.69 | 0.16 | 0.122 | 0.030 | - | 1.46 | 0.29 | | | | | | | | | | | | | | | | | | | | | | |
| Loviisa 1 | 13 | 2823 | 226 | 270 | 1.2 | 258 | - | 2.1 | 8.0 | 0.195 | 0.0016 | 0.015 | 0.0013 | ND | 0.024 | 0.069 | | | | | | | | | | | | | | | | | | | | | | |
| Loviisa 1 | 16 | 365 | 345 | 51 | 4 | - | - | - | - | 0.046 | 0.0008 | - | - | - | - | 0.13 | | | | | | | | | | | | | | | | | | | | | | |
| Loviisa 2 | 10 | 129 | 110 | 104 | 0.65 | 288 | - | 1.7 | 5.2 | 0.746 | 0.0023 | 0.038 | 0.0015 | - | - | 5.8 | | | | | | | | | | | | | | | | | | | | | | |
| Loviisa 2 | 13 | 195 | 53 | 114 | 2.3 | - | - | - | - | 0.375 | 0.0037 | - | - | - | - | 0.19 | | | | | | | | | | | | | | | | | | | | | | |
| Dukovany 3 | 7 | 2217 | 45 | 494 | 0.35 | 18 | 12 | 1.2 | 1.4 | 0.298 | 0.0023 | 0.029 | 0.0025 | ND | 0.092 | 0.13 | | | | | | | | | | | | | | | | | | | | | | |
| Paks 1 | 8 | 22 | 607 | 191 | 47 | 15 | 2.6 | 1.4 | 2.4 | 0.275 | 0.0034 | - | 0.00062 | - | - | 12.5 | | | | | | | | | | | | | | | | | | | | | | |
| Paks 1 | 9 | 82 | - | 79 | - | 49 | - | 2.6 | - | 0.299 | 0.007 | - | - | ND | 0.090 | 3.6 | | | | | | | | | | | | | | | | | | | | | | |
| Paks 2 | 7 | 26 | 62 | 147 | 3.5 | 18 | 20 | 3.1 | 1.6 | 0.177 | 0.00047 | - | - | - | - | 6.8 | | | | | | | | | | | | | | | | | | | | | | |
| Paks 2 | 8 | 46 | - | 110 | - | 28 | - | 3.4 | - | 0.163 | 0.008 | - | - | ND | 0.060 | 3.5 | | | | | | | | | | | | | | | | | | | | | | |

ND = Not determined AEA Technology 51 Cr data from filter pack




For corrosion product measurements at Sizewell B, only one of the three lines is used at any time and a pressure-rated 47 mm Millipore filter holder is connected using a "quick-disconnect" fitting. Normally a 0.45 μ m Millipore filter is used and particulate samples are collected over one to three days to ensure that sufficient material is collected for analysis (120-360 liters). The filters are analyzed by γ -spectroscopy, before being dissolved and analyzed by ion chromatography to determine the elemental transition metal concentrations. A filter stack could be placed in the Millipore holder, but might not give the best results as the optimum volumes that need to be processed for soluble and particulate species may be different. The volume analyzed is such that the small amount of exposure to air when the filter is changed has an insignificant effect.



Figure 4-3 Capillary Line Sampling Arrangement at Sizewell B

The outlet tube from the Millipore holder supplies a degassing vessel, which is sparged with helium via a glass frit to remove excess hydrogen. An air gap is essential to depressurize the sample line and the outlet is located just above the liquid level. The latter ensures that the helium flow prevents air ingress and protects the sample in the degassing vessel from oxidation. Evidence that reducing conditions are maintained is provided by the absence of brown iron oxide staining of the glass surfaces of the degassing vessel.

A sample stream for soluble species analysis is taken from outside the degassing region of the vessel, and excess sample is routed to waste. For ion chromatography a sample flow of 2-4 ml min⁻¹ is used, which is passed via a loading pump to the ion chromatograph. In normal operations a concentrator column is used and the volume sampled is up to ~1 liter, during shutdowns the volume is reduced and the minimum volume sampled is ~0.2 cm³ using a sample loop. The eluent from the ion chromatograph is used to determine the radionuclide concentrations in the samples collected.

Although ion chromatography is used at Sizewell B, other analytical methods could be used. One possibility is local collection using a concentrator column or filter stack, which will give a stable sample that can be transported off-site for analysis, followed by remote analysis after elution by, for example, ICPMS or ICPOES, stripping voltammetry, AAS or γ -spectroscopy. Irrespective of the analytical method used, it is essential that all eluents and reagents contain very low concentrations of transition metals. For Sizewell B work, standards are prepared in isothermally distilled hydrochloric acid (which can also be used as an eluent). Isothermally distilled HCl is prepared by equilibrating flasks of demineralized water and concentrated HCl in a vacuum desiccator. For Millipore filter dissolution, the filters are ashed and then the residue fused with ultra high purity potassium hydrogen sulfate.

Although in principle the Dionex ion chromatography method used at Sizewell B could be used for routine analysis, in practice the method is too labour-intensive for it to be used routinely. Instead the method is used in short measurement programs to characterize primary coolant behaviour and to make detailed measurements of elemental corrosion product concentrations during refueling shutdowns. Essentially identical methods were used at most of the PWR and VVER stations in Table 4-1, although it was not possible to fit capillary sample heads in all cases.

4.2.2 Ringhals (4, 33)

The capillary sampling lines fitted at Ringhals 2 are shown in Figure 4-4 ($\underline{4}$); very similar arrangements are used at Ringhals 3 and 4 ($\underline{4}$). While they are very similar to the system used at Sizewell B, they differ in that three AEA Technology designed single capillary heads are installed in the RCS hot leg sample lines in all three Ringhals units. One of these capillary sample lines is shown in Figure 4-5. In addition, Ringhals 2 has two additional single capillary heads installed on either side of the RCS filter in the CVCS letdown line. At all three Ringhals units there is a continuous hot leg sample bypass line running at 200 kg h⁻¹ to the volume control tank, which satisfies the requirement for a continuous high sample line flow to the capillary sample heads.

The capillary sampler lines are used for routine RCS elemental corrosion product sampling at all three Ringhals units, although there are slight differences in the procedures used. At Ringhals 2 they have been used since 1992 and at Ringhals 3 and 4 since 2000. The normal flow rate through each capillary line is 30 to 40 ml min⁻¹. One capillary head is used for normal "grab" sampling and one for integrated sampling. At Ringhals 3 and 4 the final head is used for continuous particle analysis; a similar analyzer is installed at Ringhals 2 but is only used periodically to investigate particle size distributions and transient behavior. Currently, because of the additional γ -spectroscopy work-load, RCS corrosion product radionuclides at Ringhals 3 and 4 are only measured on <50 ml "grab" samples passed through the filters and the integrated sampler is reserved for elemental corrosion product analyses. However, the individual filters are counted at Ringhals 2 (<u>31</u>).



Figure 4-4 Schematic Arrangement of the Capillary Sample Lines Installed at Ringhals 2 PWR



Figure 4-5 Arrangement of One of the Capillary Sample Lines Installed at Ringhals 2 PWR

At Ringhals integrated samples are collected over a 4-day period, equivalent to an integrated volume of 150 to 300 liters, depending on other operational demands that can affect the flow rate. During this period, valve movements in the hot leg sample line are not permitted, nor are flow rate changes, so that transients are minimized. Samples are collected in a 47 mm pressure-rated Millipore holder, containing an upper $0.45 \,\mu$ m Millipore filter on top and two Gelman cation membranes. Anion membranes are not currently used, as they become highly active and were of poor quality, but could be re-introduced. At Ringhals "quick disconnect" fittings are not permitted, since they could be crud traps.

After sampling, the holder is removed, purged and, at Ringhals 2, dried with nitrogen to remove liquid. However, the filters are not dried at Ringhals 3 and 4, without having any apparent effect on the results. The filters are stored for five to seven days to allow short-lived species to decay to improve detection limits. The filter holder is then opened and the Millipore filter and the two cation membranes measured by γ -spectroscopy to give the radionuclide concentrations. Finally, the filters and membranes are then dissolved in concentrated sulfuric/nitric acid in a microwave oven and analyzed by ICPOES to give the elemental concentrations.

Quality checks showed that 90 to 95% of corrosion products in the hot leg sample stream are retained on the filter stack components during normal operation. This was considered acceptable compared with normal sampling errors. The integrated sampling method cannot always be used during shutdowns or startups as the cation membranes become saturated. At these times in Ringhals 3 and 4 normal "grab" sampling is used, but the integrated filters are still used in Ringhals 2 (33).

Total iron, nickel and cobalt data obtained using the RCS integrated samplers over the last three years at Ringhals 2, 3 and 4 are shown in Figure 4-6. Here it may be seen that the dominant elemental corrosion product in all three units was iron at $1-2 \mu g k g^{-1}$ (ppb), followed by nickel mainly at 0.05 to 0.2 $\mu g k g^{-1}$ and then cobalt at about 0.002 $\mu g k g^{-1}$ (2 ng kg⁻¹ or ppt). These values are very similar to those for other PWRs and VVERs in Table 4-1. Figure 4-6 also shows that elemental concentrations increased greatly at shutdown and then recovered slowly in the first few months of the next cycle. It is notable that the nickel gave more scattered results, which the station attributes to the fact that there the nickel particulate fraction is higher than either iron or cobalt and is, therefore, more prone to the plant transient effects. This difference is illustrated in Figure 4-7, which gives soluble and particulate data for Ringhals 2; data for Ringhals 3 and 4 were essentially identical. As before these distributions were similar to those at other PWRs and VVERs given in Table 4-1.

It is reported (<u>33</u>) that cobalt-58 and cobalt-60 show similar behaviour to the elemental corrosion product species. This is illustrated for Ringhals 2 for total cobalt-58 and cobalt-60 in Figure 4-8, both measured on "grab" samples collected using the capillary line.



Figure 4-6

Total Iron (Blue), Total Nickel (Green) and Total Cobalt (Red) Concentrations at Ringhals 2 (Top), Ringhals 3 (Middle) and Ringhals 4 (Bottom) Over Four Fuel Cycles From 2001 to 2005





Iron (Top), Nickel (Middle) and Cobalt (Lower) Concentrations at Ringhals 2. Soluble Data in Red, Particulate <0.45 μ m in Blue and Total in Green





Figure 4-8

Total Cobalt-58 (Top) and Cobalt-60 (Lower) Concentrations at Ringhals 2 Obtained by "Grab" Sampling

5 HIGH TEMPERATURE RCS HOT LEG CORROSION PRODUCT SAMPLING AT DIABLO CANYON AND CATAWBA

Fuel clad deposits are composed of a mixture of nickel ferrite, elemental nickel, nickel oxide and, occasionally when there are thick deposits, bonaccordite (Ni₂FeBO₅). Not all of these are retained after a refueling shutdown, particularly nickel which is preferentially released during the shutdown transient. In addition, the RCS shutdown chemistry is designed to promote nickel, iron and cobalt dissolution from the deposits to allow their removal by the purification system. Due to these two factors, post-shutdown fuel crud analyses underestimate the amount originally present, and do not reflect the entire picture regarding its elemental composition and its crystal structure during power operation. However, in normal operation some circulating RCS particulate will have characteristics that are similar to those of forming the outer layer of deposits on the fuel surfaces, and this proportion increases markedly during transients. This is particularly true following control rod insertion tests and power changes, both of which release particulate from the fuel clad, see Figures 2-2 and 2-3.

The link between circulating particulate and fuel crud deposits was the original basis of the high temperature sampling program carried out at Catawba 1 and Diablo Canyon 1 ($\underline{34}$ to $\underline{36}$). For these stations a sample system was designed that, as far as was practicable, would collect a representative particulate sample during power operation. For this, the sample system was designed to:

- 1. Collect a particulate sample at the highest practical temperature, since key corrosion product species such as nickel ferrite and nickel oxide have a retrograde solubility.
- 2. Prevent exposure to air until the sample can be dried.
- 3. Operate at a continuous constant sample line flow rate, with a velocity of approximately 6 ft s^{-1} (2 m s^{-1}).
- 4. Avoid any pressure reduction devices upstream of the high temperature particulate filter, as these act as crud traps that will accumulate particulate.

As normal PWR primary coolant sampling practices do not meet these requirements, a special high temperature particulate sample system was developed.

The Diablo Canyon 1 version of the high temperature sample panel is shown in Figure 5-4; that used at Catawba 1 was very similar. Reactor coolant was drawn from the hot leg of Loop 1 and flowed continuously at approximately 2.7 liter min⁻¹ through Valves 1-280 and 1-281, before being returned to the CVCS letdown demineralizer inlet stream. At this flow rate the fluid

velocity through the sample line was 2 m s⁻¹ and the Reynolds Number was in the turbulent range. An isokinetic sample head was installed in the line to divert approximately 135 ml min⁻¹ of the sample flow to a high temperature filter (Figure 5-2), which contained either a 0.2 or a 0.4 μ m silver membrane filter operating at approximately 225°C (437°F). After filtration the sample was cooled and it was then passed through an ambient temperature filter housing containing a cation ion exchange membrane. Finally, there was a back pressure regulator. After sampling, the plan was to isolate the filters and to dry them using an argon purge before removing the membrane filter. VCR fittings were provided to enable the high temperature filter assembly to be removed from the panel (Figure 5-3) and a tool was provided to assist in removing the sintered stainless steel porous metal filter and the silver membrane from the housing. When a high temperature sample was not required, the housing could be assembled without the porous metal filter and silver membrane. In practice, only the filter housings from Catawba 1 were sealed with plugs after purge drying with argon at the plant. At Westinghouse these filters were processed in an argon atmosphere to avoid additional air exposure (<u>36</u>). At Diablo Canyon 1 the filters were not sealed before shipment and they were therefore processed without using an argon cover gas.

In the initial program (<u>36</u>) the high temperature filters were studied by a variety of solid-state techniques to identify the particulate species present. These showed that in addition to nickel ferrite of variable composition, sub-micron metallic nickel particles were a common component of the circulating particulate, but nickel oxide particulate was not present. In addition to these components, zirconium dioxide particulate was found at both stations and graphite particles at Diablo Canyon 1, the latter probably derived from the zinc acetate added to the coolant. Selected filters were also analyzed to determine their elemental and isotopic composition. For this the silver membrane filters were dissolved at 200°C in a mixture of nitric and hydrofluoric acids in a microwave oven. Hydrochloric acid was added to precipitate excess silver and the solution was analyzed by Inductively Coupled Plasma-Mass Spectrometry (ICPMS). Selected low temperature cation filters were analyzed in the same way, omitting only the hydrochloric acid addition step.

High temperature RCS samples were collected at Catawba 1 during Cycles 13 and 14 (<u>36</u>). Ten integrated high temperature filter samples were collected over periods of several days, of which four were at the end of Cycle 13, one during the Cycle 13 shutdown, one during the Cycle 14 start-up and four during Cycle 14. These studies were mainly aimed at identifying the type of particulate present on the high temperature filters (<u>36</u>) and only four filters were processed to give elemental and isotopic concentrations. In addition, only three low temperature cation filters were collected of the soluble fraction for analysis by ICPMS. In the continuation of this study at Catawba 1 (<u>37</u>) both high and low temperature filter samples collected over the same 24 hour periods were analyzed to give typical soluble and particulate concentrations, but radionuclide concentrations were not determined. Results from both programs are shown in Tables 5-1 and 5-2.

At Diablo Canyon 1 the initial program also concentrated on the nature of the particulate present in the RCS. Five integrated high temperature samples were collected in Cycle 12, but only one low temperature cation sample was collected and, unfortunately, no radionuclide concentrations were calculated (<u>36</u>). Two further pairs of samples were analyzed in recent studies (<u>37</u>). The results are also summarized in Tables 5-1 and 5-2.



High Temperature RCS Hot Leg Corrosion Product Sampling at Diablo Canyon and Catawba

Figure 5-1 Diablo Canyon High Temperature Sampler



Figure 5-2 High Temperature Filter Schematic



Figure 5-3 High Temperature Filer Housing

Compared with the data obtained using capillary hot leg samplers given in Table 4-1, the elemental data from both Catawba 1 and, with the exception of the zinc added to the RCS, Diablo Canyon 1 were similar. Not only did this include the overall concentrations, but also the distribution between the soluble and insoluble fractions. Thus, iron, manganese, zinc and cobalt were mainly present as soluble species, while nickel was more evenly divided between the soluble and insoluble fraction being higher). Chromium was only present at very low concentration in both the insoluble and soluble fractions, reflecting the fact that it mainly remains in the inner layer of the out-of-core oxides.

Less data were obtained on corrosion product radionuclide concentrations. In this case the data from Catawba 1 were similar to those from comparable plant with Alloy 600 steam generators (Doel 2 to 4, Vandellòs II and Penly 1), although the Co-60 concentrations at Catawba were low. As is apparent in the data in Table 4-1, the ratio of soluble to insoluble Co-58 and Co-60 is lower than it was for elemental cobalt. At Catawba 1 limited comparisons can also be made between the results obtained using the high temperature sampler and the normal station "grab" sample method. During the final weeks of Cycle 13 station data (34) gave filterable and non-filterable concentrations of Co-58 of between 1E-4 and 1E-3 μ Ci ml⁻¹. In August 2002 the average "grab" sample particulate concentration was 1.5E-3 μ Ci ml⁻¹. In both cases the "grab" samples were biased high by factors of the order of one hundred. Similar bias was reported for particulate Zr-95 in August 2002. A similar high bias must be anticipated whenever "grab" samples are collected without continuous flushing of the sample line.

Overall, it is clear that using a high temperature filter gave similar results to those obtained using a continuously flowing hot leg capillary sampler operating at ambient temperature, but with the sample stream filtered before being exposed to air.

Table 5-1Soluble and Particulate Concentrations at Catawba 1 and Diablo Canyon 1

| Date/Time | | Soluble (µg kg ⁻¹ , ppb) | | | | | | | Insoluble (µg kg ⁻¹ , ppb) | | | | | | |
|---|--------------------|-------------------------------------|-------|--------|-------|-------|---------|---------|---------------------------------------|-----------|--------|--------|-----------|--|--|
| Sampling Started | Collection Time | Cr | Fe | Mn | Ni | Со | Zn | Cr | Fe | Mn | Ni | Co | Zn | | |
| Catawba 1 | | | | | | | | | | | | | | | |
| 4 Mar 2002, 7 weeks to EOC 13 | 14 days | - | - | - | - | - | - | 0.002 | 0.196 | 0.003 | 0.027 | 0.001 | 0.003 | | |
| 16 April 2002, EOC 13 Coastdown | 9 days | 0.351 | 1.535 | 0.121 | 0.243 | 0.003 | 0.805 | 0.002 | 0.125 | 0.0004 | 0.028 | 0.0003 | 0.001 | | |
| 25 April 2002, Shutdown | 28.25 hours | 0.009 | 0.800 | 0.062 | 0.033 | 0.001 | 0.017 | - | - | - | - | - | - | | |
| 20 May 2002, BOC 14 from 98% power | 3.17 days | 0.009 | 1.020 | 0.050 | 0.187 | 0.004 | 0.005 | - | - | - | - | - | - | | |
| 13 June 2002, BOC 14 | 40 days | - | - | - | - | - | - | 0.003 | 0.027 | 0.0003 | 0.012 | 0.0001 | 0.0003 | | |
| 6 August 2002, BOC 14 | 14 days | - | - | - | - | - | - | 0.004 | 0.033 | 0.0003 | 0.027 | 0 | 0.0006 | | |
| 4 January 2004 18:30 | 24 hours | 0.0111 | 2.39 | 0.109 | 0.282 | - | 0.022 | - | - | - | - | - | - | | |
| 17 February 2004 08:00 | 24 hours | 0.0158 | 4.04 | 0.185 | 0.227 | - | 0.0163 | - | - | - | - | - | - | | |
| 10 May 2004 08:00 | 24 hours | 0.0119 | 5.4 | 0.222 | 0.513 | - | 0.0344 | - | - | - | - | - | - | | |
| 26 July 2004 14:30 | 24 hours | 0.0129 | 3.66 | 0.153 | 0.19 | - | 0.0185 | 0.00185 | 0.212 | <0.000514 | 0.0649 | - | <0.000514 | | |
| 27 October 2004 09:30 | 24 hours | 0.0147 | 3.33 | 0.128 | 0.186 | - | 0.0202 | 0.00242 | 0.0268 | <0.000514 | 0.0737 | - | <0.000514 | | |
| 11 November 2004 15:30 | 24 25 hours | 0.00734 | 2.95 | 0.109 | 0.18 | - | 0.018 | 0.00081 | 0.0151 | <0.000509 | 0.0184 | - | <0.000509 | | |
| 12 November 2004 18:45, during power reduction | 23.5 hours | 0.0115 | 4.33 | 0.159 | 0.578 | - | 0.0132 | 0.00604 | 0.0581 | <0.000919 | 0.282 | - | <0.000919 | | |
| 13 November 2004 21:30, during power increase | 35.5 hours | 0.183 | 4.04 | 0.149 | 0.758 | - | 0.022 | 0.00087 | 0.00933 | <0.000348 | 0.072 | - | <0.000348 | | |
| 15 November 2004 10:45 | 27.75 hours | 0.0154 | 2.8 | 0.0964 | 0.281 | - | 0.00836 | 0.00109 | 0.0101 | <0.000445 | 0.0453 | - | <0.000445 | | |
| Average at steady power | - | 0.0127 | 3.51 | 0.143 | 0.267 | - | 0.020 | 0.0009 | 0.038 | - | 0.029 | - | - | | |
| Diablo Canyon 1 | | | | | | | | | | | | | | | |
| 26 June 2003, MOC 12 | 11 days | 0.007 | 2.729 | 0.170 | 0.424 | 0.041 | 26.563 | 0.020 | 0.234 | 0.0.001 | 0.110 | 0.0004 | 0.030 | | |
| 14 July 2004 14:30 | 26 hours | 0.0162 | 2.58 | 0.232 | 0.489 | - | 6.55 | 0.0135 | 0.97 | 0.00122 | 0.37 | - | 0.256 | | |
| 26 August 2004 14:15 | 26 hours | 0.0232 | 3.49 | 0.206 | 0.264 | - | 14.8 | 0.00958 | 0.058 | 0.00074 | 0.178 | - | 0.0083 | | |
| Average at steady power | - | 0.020 | 3.035 | 0.219 | 0.377 | - | 10.7 | 0.012 | 0.514 | 0.001 | 0.274 | - | 0.132 | | |

Hatched results in 2004 obtained during power transients, others during steady state operation; averages are for 2004 steady state data.

Table 5-2Corrosion Product Radionuclide at Catawba 1

| Date/Time | | | Radionuclide | | | | | | | | | |
|---------------------------------------|--------------------|--------------------|--------------|---------|----------|---------|----------|---------------------|----------|---------|----------|---------|
| Sampling Started | Collection Time | Sample Fraction | Cr-51 | | Co-58 | | Co-60 | | Mn-54 | | Fe-59 | |
| | | | µCi ml⁻¹ | MBq m⁻³ | µCi ml⁻¹ | MBq m⁻³ | µCi ml⁻¹ | MBq m ^{-₃} | µCi ml⁻¹ | MBq m⁻³ | µCi ml⁻¹ | MBq m⁻³ |
| Catawba 1 | | | | | | | | | | | | |
| 4 Mar 2002, 7 weeks to EOC 13 | 14 days | Insoluble | ND | ND | 1.51E-5 | 0.559 | 6.61E-7 | 0.0244 | 6.98E-7 | 0.0258 | ND | ND |
| 16 April 2002, EOC 13 Coastdown | 9 days | Soluble | ND | ND | 8.60E-6 | 0.318 | 2.33E-7 | 0.0086 | 8.25E-6 | 0.305 | ND | ND |
| | | Insoluble | ND | ND | 2.11E-5 | 0.781 | 4.47E-7 | 0.0165 | 4.46E-7 | 0.0165 | ND | ND |
| 25 April 2002, Shutdown | 28.25 hours | Soluble | ND | ND | 1.60E-5 | 0.592 | 5.68E-7 | 0.0210 | 7.30E-6 | 0.270 | ND | ND |
| 20 May 2002, BOC 14 from 98% power | 3.17 days | Soluble | ND | ND | 9.26E-6 | 0.343 | 9.09E-7 | 0.0336 | 2.54E-6 | 0.094 | ND | ND |
| 13 June 2002, BOC 14 | 40 days | Soluble | ND | ND | 3.09E-6 | 0.114 | 1.93E-7 | 0.0071 | 9.77E-8 | 0.0036 | ND | ND |
| 6 August 2002, BOC 14 | 14 days | Insoluble | ND | ND | 9.82E-6 | 0.363 | 1.88E-7 | 0.0070 | 1.04E-7 | 0.0038 | ND | ND |

Results given in μ Ci ml⁻¹ and MBq m⁻³ to allow comparison with values in Table 4-1

6 CVCS LETDOWN LINE SAMPLING

A CVCS letdown line sample is usually only analyzed as one of the measurements required to determine the CVCS demineralizer decontamination factor, and it is not normally used as the main source of coolant samples for corrosion product analyses. The main reason for this is that the sample is no longer at RCS temperature and that particulate concentrations may be different due to the lower flow rate in the system. However, the low temperature is an advantage when measuring soluble corrosion product species, as the interactions with the oxides on the sample line walls that occur in the higher temperature parts of a hot leg sample line are absent. This is because any high temperature interactions occur in the CVCS regenerative heat exchanger, and will normally have reached equilibrium. Differences in particulate concentrations may be an issue, but here again it must be remembered that the CVCS letdown line flows continuously and it will tend to be in equilibrium with the particulate concentrations in the RCS itself.

At Vandellòs II problems were encountered in the use of its main sample panel (<u>38</u>), where cross-leakage occurred between RCS sample lines at 155 bar and those at lower pressure. As one of the measures to avoid cross-leakage, a separate CVCS corrosion sample panel was designed (<u>39</u>), with the intention of transferring routine corrosion product monitoring from the RCS hot leg sample line to the CVCS letdown line. A 'nominal' isokinetic sample head was fitted in the vertical line before the CVCS demineralizers to give good particulate sampling and the panel was located 5 to 10 metres from the sample take-off point. More importantly, it was decided to collect corrosion products on filters mounted in a Millipore 47 mm pressure-rated filter holder. This decision enabled the coolant to be filtered without exposing it to air, thus preserving the original distribution between the soluble and particulate fractions. In normal use the filter holder has one 0.45 μ m Gelman anion filter can be fitted, in practice an anion filter is not used as the corrosion products are only collected on the cation filter and the anion filter becomes very active if iodine isotopes are present. The sample panel installed at Vandellòs II is shown in Figure 6-1.

When used to collect a CVCS corrosion product sample (<u>39</u>), the first stage is to flush the sample system for 5 to 10 minutes at a flow rate of approximately 1 litre min⁻¹ with the filter holder in place, but with no filters installed in the filter holder. For this stage valves B, A and 5 are opened and the sample stream is allowed to flow to waste. The filter holder is then opened and the filters fitted. About 2 litres of sample are passed through the filters at a flow rate of 1 litre min⁻¹, with the actual volume recorded by the totalizer (valves B, A and 5 open during sample collection and the filter eluate is passed to the sample drains system). The filters are removed, separated and stored in individual filter holders for transfer to the laboratory. Finally, the lines in the panel are flushed with demineralized water, opening valves 2, A and 3 for about 2 minutes and then 2, A and 5 for a further about 2 minutes.

Similar panels are planned for Ascó I and 2, with the important difference that the return line to the CVCS will be omitted as there is a risk of adding demineralized water to the RCS when the sample panel is flushed. At Vandellòs II valves 6, 7 and C are locked shut to avoid this risk.

The individual filters are counted by γ -spectroscopy to give the soluble and particulate radionuclide concentrations. The cation paper is then eluted using hydrochloric acid to remove the soluble elemental fraction, while the Millipore filter is digested in Aqua Regia to dissolve the element particulate fraction. Until Cycle 13 cobalt and nickel were analyzed by stripping voltammetry and iron by graphite furnace atomic absorption spectroscopy. Since Cycle 13 elemental analyses have been carried out by graphite furnace atomic absorption spectroscopy, which because of the higher limit of detection has reduced the amount of data collected. In future it is planned to use ICPMS at Vandellòs II and ICPOES at Ascó, which will improve elemental corrosion product detection limits.

At Vandellòs II the CVCS sample panel can only be used during normal operation, as the filter papers saturate at the much higher concentrations present during refueling shutdown. The station also reports that the flow rate used of 1 litre/min is the maximum to give isokinetic sampling with the particular sample head fitted in the CVCS letdown line.

The sample panel fitted at Vandellòs II has been used for routine corrosion product sampling for the past ten years since the start of Cycle 8. Examples of the results obtained up to the end of Cycle 14 are shown in Figures 6-2 and 6-3 (<u>38</u>).









CVCS Letdown Line Sampling



Figure 6-3 Elemental Corrosion Product Concentrations at Vandellòs II Measured Using the CVCS Sample Panel

At Vandellòs II Cycles 8 to 14 cover the transition from 12-month cycles (Cycle 8) to 18 month cycles (Cycles 10 to 14) and a plant uprate by 4.5% (from Cycle 11). The primary water chemistry was a Modified Chemistry regime up to Cycle 12 and a Constant Co-ordinated Chemistry in Cycles 13 and 14. When compared with the earlier data obtained using the CRCS panel the CVCS panel results show clearly that:

- 1. The distribution between soluble and insoluble species in the RCS is very different when measured without exposure to air, and that normally soluble species predominate (compare Figures 3-1 and 6-2).
- 2. The reproducibility of the data is very greatly improved.
- 3. Systematic changes in corrosion product behaviour can be identified clearly.

Due to the better reproducibility in the measurements, the change to 18-month cycles and power uprating caused clearly identifiable changes in particulate radionuclide behaviour, which was linked to the amount of fuel crud formed in response to the changes in cycle length, boiling duty, cycle pH and the type of fuel loaded. These also affected soluble cobalt-58 concentrations and had a significant impact on soluble manganese-54 levels. Although elemental corrosion product data were not as complete, they showed similar trends.

Here, the detailed explanation of the RCS behaviour at Vandellòs II is not the main reason for describing the results obtained at this station over the last ten years. What is apparent is the quality of the data that can be obtained and the fact that where comparisons can be made the data are very comparable to those obtained using a continuous RCS hot leg sample. For example, if the elemental results are compared with those from Ringhals shown in Figures 4-6 and 4-7 it may be seen that not only are the circulating concentrations essentially identical, but that the distributions between the soluble and particulate fractions are also very similar. These facts, the detailed changes in particulate concentrations and the simplicity of the approach developed at Vandellòs II suggest that this method of corrosion product analysis would greatly improve the understanding of the problems currently being experienced in U.S. PWRs.

7 ANALYSIS METHODS

It is apparent that a wide variety of analytical methods can be used to analyze elemental and activated corrosion products. For the radionuclides the main options are to count a liquid sample, or to count a Millipore or cation filter onto which the radionuclides are held or exchanged. There is now very considerable experience in European PWRs to show that using a filter paper geometry gives very good results. When this is combined with integrated sampling and separation methods that are used before the sample is exposed to air, it will show the distribution between soluble and particulate species in the coolant (or at least that after the RCS has cooled to ambient temperature), as well as improving the overall detection levels.

The choice of a method for determining elemental concentrations is more difficult as it is linked to manpower needs and the analytical sensitivity desired. Of the methods now available ICPMS and ICPOES are probably the most sensitive and versatile, but these may not be sufficiently rapid to follow changes at shutdown on-line. For the latter, ion chromatography remains the most satisfactory option, but here the method is probably too labour-intensive to use except for special investigations. The remaining method that could be used routinely is graphite furnace atomic absorption spectroscopy, but here the sensitivity is such that some elements, such as cobalt, may not be detectable.

8 CONCLUSIONS

Measuring representative corrosion product concentrations in the RCS is a particularly difficult task, which is fraught with problems due to the way that the species interact with the oxides on the sample line walls and the way that pH and corrosion product solubility changes as the coolant flows along the sample line.

For RCS hot and cold leg samples:

- Corrosion product sampling is normally dominated by transient events that last hours or days and affect measured concentrations. Often the results can be biased high by up to one hundred times and will have a high scatter.
- The distribution between soluble and particulate fractions is modified to some extent as the sample flows down the sample line, and very significantly by iron precipitation when the sample is exposed to air before separation.
- Most manual "grab" sampling methods are very unlikely to give representative corrosion product concentrations, and if they are exposed to air before analysis, will give totally misleading indications of the soluble and particulate fractions in the primary coolant.
- The most representative "grab" samples are obtained when samples are collected using continuously flowing sample lines operating at a constant, relatively high flow rate, and when they are separated or analyzed *in situ* in a way that prevents exposure to air and gives a stable sample form.
- Capillary sample lines are a simple method of obtaining continuous samples, but they are not essential and a continuously flowing normal sample line can be used successfully.
- A number of alternative methods of integrated sampling and analysis are possible and have been used in European stations. A similar integrated sampler has been developed in the U.S., although its original function was to collect RCS particulate before the distribution was modified as the sample stream cooled.
- Capillary RCS hot leg integrated samplers are used very successfully at Ringhals for routine corrosion product analysis.

Notwithstanding the very many problems associated with obtaining a representative corrosion product sample from an RCS hot or cold leg, successful measurements should still be possible. However, for this to occur, a practicable requirement for making successful and meaningful measurements must exist. A possible set of requirements is as follows:

Conclusions

- 1. RCS hot or cold leg samples should be collected in a way that gives results that will reflect systematic changes in RCS corrosion product behaviour. The results obtained do not need to be totally representative of the true distribution between soluble, colloidal and particulate in the RCS itself, but they must be reproducible and give interpretable data from which changes in behaviour can be deduced.
- 2. If measurements are required of the separate soluble and particulate fractions in the sample that is collected, then the sample must be filtered without exposure to air. Exposure to air precipitates iron (III) hydroxide, which will scavenge other soluble radionuclides by co-precipitation. Iron (III) hydroxide precipitation will greatly increase the apparent particulate fraction of all radionuclides in the measured sample.
- 3. Conventionally, soluble and particulate fractions are separated into a "soluble" and a "particulate or insoluble" fraction, based on their ability to pass through or be retained on a 0.45 μ m Millipore or similar filter paper. In practice the soluble fraction always includes the true soluble fraction, any colloids and smaller particulate, some of which may have dissolved during sampling. The particulate fraction will only include the larger particulate species.

Due to the very great difficulties that exist in PWRs that cannot use a continuously flowing RCS hot or cold leg sample line, an alternative would be to use the CVCS letdown line as the source of the corrosion product sample. It has been argued that a CVCS letdown sample is not representative of the distribution in RCS, but experience at Vandellòs II suggests that this is not correct.

At Vandellòs II, data collected over ten years indicates that:

- Very reproducible soluble and particulate corrosion product concentrations can be measured during normal operation.
- Measured concentrations were very similar to stations using continuous RCS capillary sample systems to measure corrosion product concentrations.
- Systematic changes in particulate concentrations were observed that correlated with changes in shutdown releases, increases in radiation fields and the observation of increased amounts of fuel crud.

Due to the success of the methods used at Vandellòs II, the basic simplicity of the CVCS sample panel and the probability that a similar approach could be used in most PWRs, it is suggested that all PWRs should evaluate using the method developed at Vandellòs II.

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