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Steam Generator Management Program: PWR Steam Generator Deposit Characterization Sourcebook

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Steam Generator Management Program: PWR Steam Generator Deposit Characterization Sourcebook

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EPRI Project Manager
R. Wolfe

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ELECTRIC POWER RESEARCH INSTITUTE
3420 Hillview Avenue, Palo Alto, California 94304-1338 ▪ PO Box 10412, Palo Alto, California 94303-0813 ▪ USA
800.313.3774 ▪ 650.855.2121 ▪ askepri@epri.com ▪ www.epri.com

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THE FOLLOWING ORGANIZATION, UNDER CONTRACT TO EPRI, PREPARED THIS REPORT:

Dominion Engineering, Inc.

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The following organization, under contract to the Electric Power Research Institute (EPRI), prepared this report:

Dominion Engineering, Inc.
12100 Sunrise Valley Drive, Suite 220
Reston, VA 20191

Principal Investigators
M. Little
D. Brown
R. Varrin

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ABSTRACT

The management of corrosion product deposition on the secondary side of PWR steam generators is an ongoing challenge facing the nuclear power industry. The buildup of deposits in steam generators can accelerate tubing degradation, even in replacement steam generators tubed with corrosion resistant alloys. Further, deposits can reduce heat transfer efficiency and/or disrupt normal thermal hydraulics, leading to issues such as vibration-induced wear and water level instabilities. Periodic collection and characterization of deposits is important for monitoring the condition of the secondary side of steam generators and for planning maintenance activities designed to remove these deposits. This sourcebook provides detailed information on how to collect and characterize steam generator deposits.

Keywords
Deposit characterization
Corrosion products
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SGMP

EXECUTIVE SUMMARY

Deposit characterization refers to laboratory analyses performed to determine the chemical and physical properties of corrosion products and impurities that accumulate in the secondary side of steam generators. Guidance for performing steam generator deposit characterizations was previously published in EPRI Report TR-106048: *Characterization of PWR Steam Generator Deposits*, which also provides considerable background on the formation, transport, nature, and effects of steam generator deposits. This sourcebook discusses the latest practices being utilized to collect and characterize steam generator deposits, and serves as an update and supplement to TR-106048. Efforts were made in this sourcebook to update and provide greater focus on practical recommendations for collecting and characterizing steam generator deposits, while limiting background discussion pertaining to deposit formation and effects since those portions of TR-106048 have since been updated and expanded in later EPRI documents referenced herein. It is anticipated that this sourcebook will serve as a useful reference for utilities issuing procurement specifications for steam generator deposit collection (for example, during sludge lancing) or deposit characterization services, and/or for utilities attempting to collect and characterize steam generator deposits themselves.

ACRONYMS

AAS	Atomic Absorption Spectroscopy
AES	Atomic Emission Spectroscopy
ASCA	Advanced Scale Conditioning Agent
ATEM	Analytical Transmission Electron Microscopy
AVT	All-Volatile Treatment
BET	Brunauer-Emmett-Teller
BKD	Backscatter Kikuchi Diffraction
BSE	Backscattered Electrons
DCP	Direct Coupled Plasma
DEI	Dominion Engineering, Inc.
DMT	Deposit Minimization Treatment
EBSD	Electron Backscatter Diffraction
EDS	Energy Dispersive Spectroscopy
EFPY	Effective Full Power Years
EPRI	Electric Power Research Institute
ESCA	Electron Spectroscopy for Chemical Analysis
FDB	Flow Distribution Baffle
FME	Foreign Material Exclusion
FOSAR	Foreign Object Search and Retrieval
FTIR	Fourier Transform Infrared
ICP	Inductively Coupled Plasma
ID	Inner Diameter
IGA	Intergranular Attack
IQS	Instituto Químico de Sarrià
IR	Infrared
IX	Ion Exchange

MS	Mass Spectrometry
NDE	Non-Destructive Examination
OD	Outer Diameter
OES	Optical Emission Spectrometry
OTSG	Once-Through Steam Generator
PWR	Pressurized Water Reactor
RSG	Recirculating Steam Generator
SCC	Stress Corrosion Cracking
SEM	Scanning Electron Microscopy
SGOG	Steam Generator Owners Group
SG	Steam Generator
SIMS	Secondary Ion Mass Spectrometry
TEM	Transmission Electron Microscopy
TSP	Tube Support Plate
TTS	Top-of-the-Tubesheet
WDS	Wavelength Dispersive Spectroscopy
XPS	X-Ray Photoelectron Spectroscopy
XRD	X-Ray Diffraction
XRF	X-Ray Fluorescence

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BACKGROUND AND INTRODUCTION

The gradual erosion and corrosion of the feedwater, condensate, steam and drain systems at a pressurized water reactor (PWR) nuclear plant results in the liberation of corrosion products from system surfaces and into the secondary cycle. Additional contaminants and impurities are introduced into the secondary side of the plant with the makeup water, auxiliary feedwater, and as a result of condenser leaks. Those materials which are not filtered or removed from the feedwater by condensate polishing can eventually be transported to the steam generators (SGs). If not removed from the SGs by the blowdown system, these materials can deposit on SG internal surfaces. The buildup of deposits within the SGs may lead to a number of undesirable side effects, including accelerated tubing degradation, reduced heat transfer efficiency, and/or disrupted thermal hydraulics (e.g., vibration-induced wear, tube fatigue, water level instabilities, etc.). The likelihood for each of these to occur depends on the quantity, distribution, and properties of deposits. Thus, periodic collection and characterization of deposits is an important activity performed in support of overall SG management, and utilities regularly perform deposit characterizations to support a number of objectives, including: (1) monitoring the condition of the secondary side of the SGs[1], (2) diagnosing material degradation issues and/or thermal performance changes, and (3) planning maintenance activities designed to remove secondary side SG deposits.

Guidance for characterizing SG deposits was previously issued in EPRI Report TR-106048, which was published in 1996. Since that time there have been significant developments in plant operational practices and experiences, and advances in deposit characterization and management techniques. Therefore, it was determined that a revision to prior guidance was warranted, and this sourcebook was prepared to update and supplement TR-106048. Key industry events and trends that have affected deposit characterization and deposit management practices were considered in the preparation of this sourcebook, including:

- Widespread replacement of Alloy 600MA tubed SGs with more corrosion resistant alloys (e.g., Alloy 600TT, Alloy 690TT and Alloy 800NG). Despite the use of these more corrosion resistant alloys, deposit-related SG degradation continues to be an issue for PWRs. Notable recent examples include:
  - Three significant tube leaks at Cruas 1 (February 2004) and Cruas 4 (November 2005 and February 2006) attributed to vibration-induced wear resulting from SG deposits having partially blocked tube support plate (TSP) quatrefoils. (Both of these units have SGs with Alloy 600TT tubing.) These events led to an extensive campaign to model, characterize, and remove such blockages at EDF units [2, 3].

[1] Monitoring deposit properties such as the thickness and composition (including concentration of deleterious species such as copper and lead), along with other data such as impurity transport via feedwater, scale profiling and TTS sludge height, provides a means to estimate the overall mass of deposits present in the SG and to assess the potential corrosion risk associated with these deposits.

  - Occurrences of top-of-the-tubesheet (TTS) denting at plants with Alloy 690TT, 600TT, and 800NG tubing, as well as stress corrosion cracking (SCC) associated with denting at plants with 600TT and 800NG tubing. As discussed in detail in Reference [4], the location of TTS dents is highly correlated with the location of hard TTS deposits or "collars." These events and associated evaluations highlight the fact that despite improved water chemistry control and relatively low overall deposit inventories, TTS collars can lead to tubing corrosion, even if the build-up or hard sludge at the tubesheet is relatively small [5]. As a result, TTS collars have received significantly increased attention during recent deposit characterization and deposit removal campaigns, despite representing only a relatively small fraction of the total mass of deposits in the SGs.

- Improvements in water chemistry (and consequently lower overall deposit accumulations) have driven the development of new SG deposit management techniques and changes in deposit management philosophies at some utilities. Notable recent examples include:
  - Reduction in sludge lancing frequency at some units due to relatively low mass removals. However, possible risks associated with reducing the sludge lancing frequency have been identified, including the potential for greater consolidation of TTS sludge, and/or the possibility that foreign objects may be left behind in the SGs and lead to tube damage [6]. Thus, many utilities continue to perform sludge lancing every outage, and characterize deposits collected during sludge lancing operations in order to assess these and other risks.
  - Development of "soft" chemical cleaning techniques designed to proactively manage deposit accumulations, reduce TSP blockage levels and beneficially modify tube scale structure to improve heat transfer [7, 8]. To forecast the heat transfer benefits expected to result from a "soft" cleaning, SG tube scale can be collected prior to the outage at which "soft" cleaning is planned, and characterized before and after exposure to a simulation of the proposed "soft" cleaning process in laboratory testing. Heat transfer benefits can then be projected based on the tube scale structural changes observed as a result of the "soft" cleaning exposure using heat transfer models [9, 10]. Predictive models for thermal performance changes are based predominantly on operating history, estimates of steam generator deposit loading, and deposit properties before and after "soft" cleaning. These models have continued to be improved and refined, and heat transfer changes predicted by these models are typically in good agreement with actual plant results (e.g., observed steam pressure increases) following "soft" cleanings.
  - Development of dispersants to reduce corrosion product deposition in the SGs by enhancing blowdown efficiency [11, 12, 13]. As discussed in the Dispersant Application Sourcebook, it is suggested that utilities collect and characterize SG deposits when injecting dispersants to evaluate possible deposit changes [14]. To date, limited data exists regarding the effect of dispersants on deposit properties. Nonetheless, dispersants have generally been an effective SG deposit management tool when used independently and in combination with other SG maintenance activities.

- Replacement steam generators have typically only been operated on all-volatile treatment (AVT) water chemistry, significantly changing the nature of the sludge pile relative to original steam generators that had been operated on phosphate chemistry.

In addition to the events and trends summarized above, which have impacted the manner and degree to which utilities obtain and utilize deposit characterization data, there have been significant advances in deposit characterization techniques, including the development of new analytical techniques such as analytical transmission electron microscopy (ATEM). Further, deposit characterization vendors have developed significantly larger databases of deposit characterization information, which allow for more robust interpretation of unit-specific SG deposit properties in the context of industry experience.

This sourcebook is intended to address the changes in industry perspective and experience summarized above, and was prepared based on an updated industry survey and a review of literature published since the issuance of TR-106048. Additionally, input from deposit characterization vendors was obtained to ensure that the latest industry experience and practices were accurately reflected in this sourcebook.

Another significant change made in this sourcebook is that much of the background discussion that previously existed in TR-106048 has been removed and replaced with references to EPRI documents where this background information now exists in updated/expanded form. (In some cases (e.g., when information does not exist in other EPRI documents), background discussion has been updated and retained in appendices.) This change was made to avoid potentially conflicting information and to allow for greater focus on practical guidance for collecting and characterizing steam generator deposits. It is anticipated that this sourcebook will serve as a useful reference for utilities issuing procurement specifications for steam generator deposit collection (e.g., during sludge lancing) or deposit characterization services, and/or for utilities attempting to collect and characterize steam generator deposits themselves.

The remainder of this report is organized as follows:

- Section 2 provides guidance for collecting SG deposits, including collection techniques and frequency, as well as considerations for handling and storing deposit samples.
- Section 3 provides guidance for characterizing SG deposits, including sample preparation and analytical techniques.
- Section 4 discusses data interpretation and other considerations such as the manner in which deposit characterization results will be utilized (e.g., in preparation for SG cleaning application, as a diagnostic for assessing thermal performance losses or material degradation, etc.).
- Section 5 reviews the results of the industry survey on deposit characterization practices, and recent literature review. A copy of the utility questionnaire that was distributed as part of this survey is included as Appendix A.
- Section 6 provides a list of references.

- Background information on deposit transport and formation, the nature of SG deposits and the effects of SG deposits is included as Appendix B, C and D. Additional background reflecting recent studies on the formation and consequences of SG deposits can be found in References [5, 15, 16, 17, 18, 19, 20].

Figure 1-1 illustrates the overall process of SG deposit collection and characterization, which is discussed in the remainder of this sourcebook.

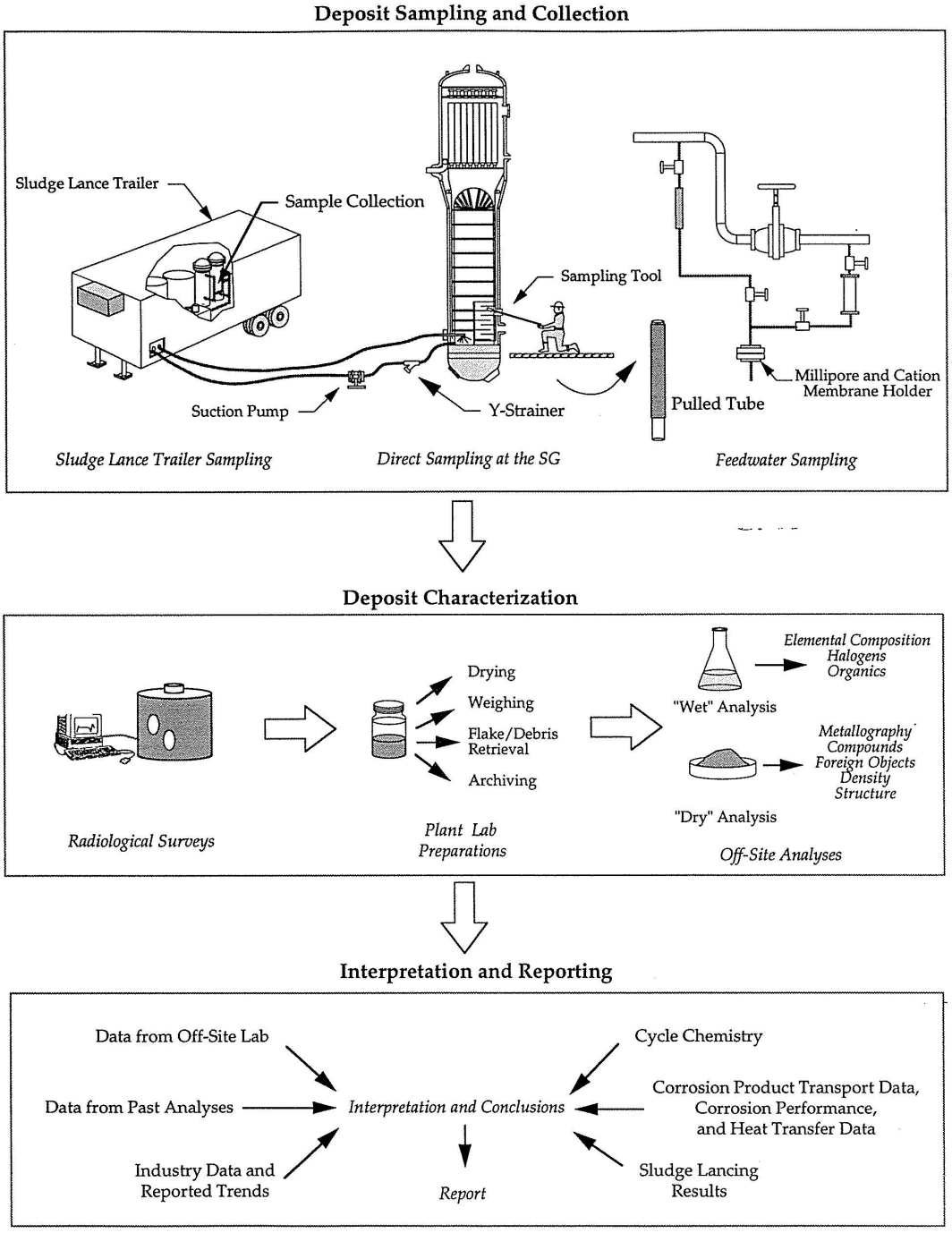

Figure 1-1
Overview of SG Deposit Collection and Characterization Activities

2
STEAM GENERATOR DEPOSIT COLLECTION

Proper collection and handling of steam generator deposits is critical for ensuring that useful and representative deposit samples are obtained and for ensuring that deposit properties are not altered during the time between deposit collection and characterization. Section 2.1 discusses deposit collection methods. Section 2.2 discusses general considerations related to deposit collection and handling. Guidance for characterization of deposit samples collected from SGs is provided in Section 3.

2.1 SG Deposit Collection Methods

While there are many techniques for collecting SG deposits, collection of deposits during sludge lancing is by far the most common. Detailed guidance for collecting representative SG deposit samples during sludge lancing is provided in Section 2.1.1. Section 2.1.2 reviews other techniques that may be used to collect deposit samples.

2.1.1 Sludge Lancing

Collection of SG deposits during sludge lancing is the most common method of obtaining deposit samples. Because sludge lancing is routinely performed during refueling outages, collecting deposits at this time provides an opportunity to collect SG deposit samples without affecting the outage schedule or increasing personnel dose. Additionally, due to the fact that foreign objects and deposits exfoliated from surfaces throughout the SG can settle on the TTS, several different types of deposits can be collected simultaneously during sludge lancing (see additional discussion of deposit types in Section 3.1.3). The main drawback of deposit collection during sludge lancing is that information regarding the precise location within the SG from which any particular deposit piece originated cannot be determined.

Deposit samples are typically collected on full-flow filters used during the sludge lancing operation. Some useful information can be obtained through the characterization of these deposit samples, and characterization of this material should be performed, if available. However, deposit material collected on sludge lancing filters is often pulverized or powdered sludge that is too small to draw meaningful conclusions in regard to the source or structure of the original deposit piece. As such, attempts should be made to collect larger deposit material during sludge lancing operations for deposit characterizations.

All sludge lancing vendors typically make use of a grit screen (or, less commonly a coarse y-strainer or basket filter) on the return line from the SGs to the sludge lancing trailer. Such straining devices are primarily used to protect sludge lancing equipment from large foreign objects (such as screws, bolts, etc.) which may be removed from the SGs when the sludge lancing water is drained. In practice, these straining devices also serve to collect a majority of the larger deposit material (such as tube scale pieces and TTS collars) during sludge lancing activities, if the screen is fine enough. This larger deposit material typically has the most value

for characterization purposes because the physical structure of the deposit pieces is preserved and can be more easily assessed. Note that it is desirable, but not always practical, to collect deposits upstream of the sludge suction pumps to minimize disruption of the structure of the deposits.

The following guidance is provided to ensure that useful and representative deposit samples are collected during sludge lancing:

- In some cases, the y-strainer or grit screen used by the sludge lancing vendor is too coarse to collect an adequate quantity of useful deposit material (sieve openings of up to 0.25 inches (~6 mm) have been used). It is recommended that utilities verify with the sludge lancing vendor that a y-strainer or grit screen with a maximum opening of about 0.04 inches (1 mm) is used within the sludge lancing system. A mesh number of 10 is acceptable, but a finer mesh, up to 18, is preferable. This finer mesh straining device could be used in lieu of or in addition to a straining device with a larger sieve opening (i.e., that is used to prevent larger foreign objects such as screws and bolts from entering sludge lancing equipment). For example, a finer mesh screen can be placed on top of the normal grit screen. Some sludge lancing vendors note that they use a larger mesh size (e.g., with 0.125-inch openings) than recommended above to prevent clogging and frequent grit screen cleaning. Although grit screen clogging has generally not been reported to be a significant issue, it is understood that some optimization of the grit screen size may be warranted on a plant-specific basis to balance effective deposit sample collection and efficient sludge lancing operation. For example, a plant which has difficulty collecting useful deposit samples (e.g., due to small deposit particle size or low deposit mass) may require a finer mesh grit screen than a plant at which large masses of useful deposit pieces are routinely collected in the grit screen during sludge lancing.
- Contamination of SG deposit samples by SG deposits from the previous sludge lancing campaign (i.e., at another plant site) has also been observed. This occurs when filters, y-strainers, grit screen, tanks, or other sludge lancing equipment are not adequately flushed or cleaned between sludge lancing campaigns at successive units. Therefore, it is recommended that utilities verify the sludge lancing vendor's procedure for cleaning the sludge lancing trailer and auxiliary equipment before and after each sludge lancing campaign. In general, it is recommended that all sludge lancing vendors complete the following activities after each sludge lancing operation (prior to leaving the site): (1) thoroughly clean and rinse all equipment, including y-strainer and grit screens and (2) remove or replace all filters, as appropriate. It is also recommended that all sludge lancing equipment, including y-strainers and grit screens, be inspected for cleanliness upon arrival at the next plant site.
- It is often useful to have as much information as possible about the location in which the deposit originated. Therefore, it is recommended that samples be collected during individual passes (or at least separately for the hot leg and cold leg sides) for each steam generator. This may involve making provisions for additional filters or having a spare grit screen available so that collection of deposits and replacement/cleaning of the filters or grit screen does not affect the lancing schedule. Careful separation of samples is very important when local information on deposit characteristics is desired, such as when a degradation phenomenon

has only been observed on the cold leg or when different SGs have different operating or deposit removal histories. Additionally, if multiple sludge lance passes are performed, samples from the first sludge lance pass may be more representative of recent deposit accumulation while samples from the last pass may be more representative of older deposits.

Additional guidance and considerations for collection and handling of SG deposits is provided in Section 2.2.

2.1.2 Other Deposit Collection Techniques

The overwhelming majority of guidance provided in this sourcebook pertains to the ex-situ characterization of SG deposits collected during sludge lancing. As noted above, SG deposit collection during sludge lancing is by far the most common practice for collecting SG deposits because it requires minimal additional time and resources (relative to sludge lancing alone), and because it yields deposit samples that are useful for many different purposes (e.g., root cause evaluations for material degradation issues, preparation for SG chemical cleaning, etc.). That said, other methods for deposit collection may be used for specific purposes, and these methods are discussed briefly below.

2.1.2.1 Specialized Sampling Tools

Steam generators typically have a number of handholes and inspection ports which provide access to the specific areas within the SG (e.g., the tubesheet, some or all of the tube support plates, etc.). Deposit samples can be manually collected through these access ports by utilizing specialized sampling tools (e.g., a reach rod with a rare earth magnet on the end), or, in the case of the tubesheet region, through the adaptation of foreign object search and retrieval (FOSAR) equipment with a deposit collection attachment (e.g., a gripper, a suction device, etc.). The main advantage of this sampling technique is that it provides precise information regarding the location from which the sampled deposits were collected, which may be beneficial for investigating local phenomena. The main drawbacks are the relative difficulty of collecting sufficiently large samples and the increased level of effort and personnel dose required to collect the deposits.

2.1.2.2 Pulled Tube

Following the removal of a tube from the steam generator, SG deposits can also be collected by scraping the outer diameter of the pulled tube or by deforming the tube to exfoliate the deposits [21]. Additionally, after a tube is pulled it may be possible to collect a SG deposit sample from the TTS through the hole created in the tubesheet prior to plugging. All of these options can provide information regarding the local environment experienced by the pulled tube, which can help identify the root cause of tubing degradation. Once deposits are collected during tube pull operations (or removed from the pulled tube after these operations), the same analytical techniques discussed in Section 3 of this sourcebook may be used to characterize these deposits. Additionally, some of these techniques (e.g., ATEM) may be used directly on the pulled tube during destructive examinations (see additional discussion in Section 3.3.5).

2.1.2.3 Feedwater Sampling

Feedwater filters can be installed during operations to collect particulate material being transported to the SGs, which may be beneficial in identifying the source of deposit materials. It is recommended that feedwater filters with a rating of 0.1 μm (0.004 mils) or smaller be used, as most particulate material transported into the generators is expected to have a diameter on the order of approximately 0.1 to 3 μm (0.004 to 0.12 mils) and it is desirable to collect the full range of particulate sizes. The primary drawbacks of feedwater sampling is that the mass of deposits collected is generally low and no direct information pertaining to actual deposits present within the SGs is obtained (although characterization of feedwater deposits may provide information that complements the characterization of actual SG deposits).

2.2 Additional Considerations for SG Deposit Collection and Handling

2.2.1 Shipping and Handling

The following guidance should be considered during and after SG deposit collection:

- As soon as practical following collection, samples should be transferred to appropriately-labeled sample bottles. At a minimum, labeling should include the following:
  - Plant name and unit number
  - Sample description (e.g., Sludge Lancing Pass A, SG-2 Hot Leg)
  - Approximate mass
  - Refueling outage number
  - Sample collection date
- Wide-mouth, high-density polyethylene (HDPE) bottles are generally appropriate for deposit collection and storage (see Figure 2-1 and Figure 2-2). Typically, 1-L bottles are used for each sample, although the size may vary depending on the quantity of deposits collected. Care should be taken to exclude any material which may contaminate the deposit sample (e.g., bottles should be rinsed with deionized water prior to use, paper inserts which may contain organic contaminates should not be used in container lids, etc.).
- Following collection, deposit samples are generally present as wet, aerated samples (although residual hydrazine from SG layup may be present in some cases depending on the timing of deposit collection). At low temperatures, the structure and composition of SG deposits is quite stable at these conditions such that no special measures (e.g., drying) are required prior to shipment of as-collected deposit samples to an off-site laboratory for deposit characterization services (or prior to performing on-site characterization). Specifically, at temperatures less than 60°C, no appreciable conversion of deposit species typically found in SG deposits (e.g., magnetite, copper metal, etc.) to more oxidized forms (e.g., hematite, copper oxide, etc.) is expected to occur for typical storage times [22, 23]. Nonetheless, up to 300 ppm hydrazine (or another suitable other oxygen scavenger such as carbohydrazide) may be added to deposit samples to ensure that deposit species remain in reduced forms, particularly if extended storage is anticipated prior to deposit characterization.

- Even if there are no immediate plans for characterization of deposit samples collected during sludge lancing or other activities, it is recommended that deposit samples be stored in labeled bottles (as described above), and archived for as long as practical (see Section 2.2.4 for additional guidance on archiving SG deposits). As noted above, the structure and composition of SG deposits are stable at low temperature, even during periods of extended storage [22, 23]. As such, meaningful SG deposit characterizations may be performed at a later time, if needed (e.g., in support of emergent material degradation issues). These archived deposit samples could also be later characterized to assess how deposit properties (e.g., thickness, porosity, etc.) have evolved over time, which may serve as an important input to a utility's overall deposit management strategy.
- Although not required, if deposit samples are dried prior to shipment to an off-site laboratory for deposit characterization services (or in preparation for on-site characterization), drying should be performed in accordance with Section 3.2 to prevent any compositional changes during the drying process.
- Prior to shipment, an integrated gamma scan must be also performed on deposit samples to determine the total activity and the activity for each isotope present in the samples (e.g., ^{58}Co, ^{60}Co, ^{54}Mn, ^{134}Cs, ^{137}Cs, etc.) to determine shipping requirements. Further, the receiving laboratory must confirm that the activities are acceptable (i.e., within the limits of the laboratory's radioactive materials handling license) prior to shipment. SG deposit samples typically have activities in the range of 10^{-5} to 10^{-2} μCi/gram for the isotopes listed above.
- If the activity of the samples is below the limit of detection, it is possible that the samples may be considered free-releasable, in which case they may be shipped as non-radioactive material with no special packaging or marking requirements. Even if SG deposit samples contain low levels of radioactivity, they can generally be shipped using a standard commercial carrier (e.g., FedEx, DHL, etc.) as "excepted packages containing limited quantities of Class 7 (radioactive) materials" in accordance with 49 CFR 173. In addition to gamma scanning to confirm that the activity of the shipment does not exceed the limited quantity limits specified in these regulations, it must also be confirmed that the radiation level at any point on the external surface of the shipping container does not exceed 0.005 mSv/hr (0.5 mrem/hr). Assuming these and other requirements of 49 CFR 173 are met, the shipping container is exempt from further marking, with the exception that it must contain a UN2910 label identifying it as an excepted package containing limited quantities of Class 7 (radioactive) materials in accordance with 49CFR172, Subpart B. Examples of suitably-labeled containers used to ship SG deposit samples are shown in Figure 2-3.

Figure 2-1
As-Collected SG Deposit Samples

Figure 2-2
Typical Nature of As-Collected SG Deposit Samples

Figure 2-3
Example Shipping Containers for SG Deposit Samples

2.2.2 Frequency of Deposit Collection

As deposit collection during sludge lancing is expected to have minimal to no impact on the sludge lancing schedule, it is recommended that these samples be collected during each sludge lancing campaign, and retained even if there are no immediate plans for deposit characterization. Other deposit collection methods (see Section 2.1.2) have greater personnel requirements and therefore should typically only be employed when sludge lancing samples are inadequate or unavailable. As discussed in Section 2.1.1, the main drawback of deposit collection during sludge lancing is a lack of precise information about the location(s) in the SGs from which the deposits originated. However, deposit characterization vendors can generally identify deposit types based on size and structure, which provides substantial value in the context of root cause evaluations, such as for TTS denting, and SG chemical cleaning preparations. Therefore, other sampling techniques are generally employed only when investigation of highly localized phenomena is needed.

The properties of deposits in a SG generally evolve gradually over time (see Section C.3.2). As such, deposits collected and characterized at any given refueling outage are generally similar in composition and structure to those collected several cycles earlier. Possible exceptions include: following significant ingress of contaminants, following major plant changes (e.g., replacement of copper-bearing materials in balance-of-plant systems), after a SG chemical cleaning application, and/or in new SGs, when deposit properties may be altered or may change more rapidly.

Based on the above, increasing the frequency of sludge lancing solely to increase the frequency of deposit collection is generally not considered to be warranted. However, it is generally desirable (although not imperative) to collect and characterize SG deposits during a recent refueling outage when preparing for a SG chemical cleaning (or other maintenance activities) such that the latest deposit characteristics can be considered in the design and qualification of the cleaning process. Therefore, some modification to the regular sludge lancing schedule may be considered to ensure that deposit samples are collected within 1 to 2 outages of the planned SG chemical cleaning application. Additional samples may also be collected just after SG chemical cleaning (or other maintenance activities), or after 1 additional cycle of operation, in order to assess the impact of the cleaning process on the deposit characteristics.

2.2.3 Required Mass of Deposit Samples

There are no specific requirements for the mass of SG deposits that must be collected to support a deposit characterization. However, in general, obtaining larger masses of deposits increases the likelihood that the overall objectives of the deposit characterization will be met. It is also important to understand that the useful material present within a deposit sample (e.g., typically the tube scale and TTS collars) may only represent a small percentage of the overall mass. Thus, the quality of the sample, and not just the overall mass, must be considered.

Based on the considerations above, the following general guidance is provided in regard to the mass of deposit samples:

- When practical, all deposit samples collected should be retained or sent to an off-site laboratory for characterization (see Section 2.2.4 for additional guidance on archiving SG deposits). Vendors that provide deposit characterization services can separate as-collected deposit samples into different deposit types and extract out the useful material (see additional discussion in Section 3.1.3). Any material that is not needed (e.g., large quantities of powdered sludge) can then be stored, discarded or returned to the utility, as appropriate.
- If the mass of deposit samples is so large that retention or shipment of all collected material is impractical, it is generally recommended that utilities retain or ship deposit samples that contain the largest deposit fragments, such as those collected on the grit screen. Consistent with guidance provided in Section 2.1.1, these samples tend to contain larger percentages of deposit types that facilitate more meaningful deposit characterization studies, such as those which might be performed in preparation for a chemical cleaning application or as part of a root cause investigation for TTS denting. A portion of the bulk powdered sludge present in deposit samples may also be retained.
- In general, a mass of 50–100 g or higher is desirable for each deposit sample. This may be easily achieved when deposit samples are obtained during sludge lancing. However, it may be more challenging when using specialized tools to extract small quantities of deposits from specific locations within the SG. Despite the much smaller masses expected for such samples (order 1 g or less), they may still be extremely useful for deposit characterization purposes.

- If deposit samples will be used in laboratory testing to qualify a chemical cleaning process to be applied at the unit of interest, it is generally desirable to obtain on the order of 100–1000 g of tube scale and TTS collars since these deposit types generally account for a majority of the deposit mass within the SG and are typically the primary deposit types which utilities seek to remove or structurally modify during SG cleaning processes. While there is no way to ensure that deposit samples will contain a specific mass of desired deposit types, the guidance provided above and previous sections (e.g., retention of all deposit samples, particularly larger deposit pieces found in grit screen samples), increases the likelihood that a sufficient quantity of useful deposit material will be obtained.

2.2.4 Archiving

As noted above, SG deposit samples collected during sludge lancing or other activities should be retained and archived for as long as practical even if there are no immediate plans for characterization of the deposit samples (see Section 2.2.1 for guidance on storage of SG deposit samples). While the recommended archival period may depend on plant-specific objectives and considerations, general guidance regarding archiving is as follows:

- Because characterization of SG deposit may be beneficial for diagnosing emergent SG issues (e.g., tubing degradation, thermal performance losses, etc.), it is generally recommended that deposits from the last three (3) deposit collection campaigns be retained (if these deposits are not characterized in accordance with Section 3 of this sourcebook).
- Longer archival periods may be appropriate in some cases. For example, if a unit is experiencing active tubing degradation (e.g., denting), foreign material ingress, or off-normal sludge chemistry trends, all SG deposit samples collected should be retained until the issue(s) are resolved. Similarly, if a utility is contemplating SG chemical cleaning, all deposit samples should be retained until the cleaning application is successfully completed.
- As noted above, if the mass of deposit samples is so large that retention or shipment of all collected material is impractical, it is generally recommended that deposit samples containing the largest deposit fragments (such as those collected on the grit screen during sludge lancing) be retained.
- SG deposit samples may be stored on-site by the utility, or at an off-site location (e.g., by the SG deposit characterization vendor). As discussed in Section 2.2.1, samples should be appropriately labeled to ensure traceability.

3
STEAM GENERATOR DEPOSIT CHARACTERIZATION

This chapter discusses the process of SG deposit characterization, including both preparation and analysis of deposit samples. Numerous techniques for characterizing the physical and chemical properties of deposits exist. The options utilized during any particular characterization process will depend on the specific utility objectives, and the nature and amount of the available deposits. As noted previously, this sourcebook focuses on the ex-situ characterization of deposits removed from PWR SGs, but related activities such as pulled tube examinations are discussed briefly, as appropriate (see Section 3.4).

This chapter is organized as follows:

- Section 3.1 discusses sample preparation activities.
- Section 3.2 identifies activities and techniques utilized during most SG deposit characterization studies.
- Section 3.3 discusses additional analytical techniques that are less common, but may be used to obtain additional SG deposit information.
- Section 3.4 discusses activities that are related to SG deposit characterizations, but that are not discussed in detail in this sourcebook due to their peripheral relevance.

As discussed in Section 4, the exact scope of work and data interpretation for data characterizations depends on utility-specific objectives. Thus, although the techniques discussed in Section 3.2 are suitable for most deposit characterizations, additional analyses such as those discussed in Section 3.3 may be appropriate in some cases. For example, if a unit has experienced condenser leaks resulting in ingress of significant quantities of contaminants, it may be beneficial to perform ion chromatography for leachable ions (e.g., $SO4^{2-}$, Cl^{-}, etc.) as part of the deposit characterization, whereas this analysis may not be of interest for other utilities. Thus, no firm recommendations are given in this sourcebook regarding techniques that should be used during all deposit characterizations. Rather, deposit characterization techniques are discussed for informational purposes (including identification of when these techniques may be useful), and the discretion is left to utilities and their selected deposit characterization vendor to determine the appropriate scope of services for their specific objectives.

3.1 Sample Preparation

As discussed in Section 2, SG deposit samples are typically received as wet, aerated samples that contain a mixture of SG tube scale, TTS collars, powdered sludge and foreign objects. These different deposit types are of interest for different reasons. For example, heat transfer performance depends primarily on tube scale properties. Thus, a utility investigating thermal performance losses may be primarily interested in tube scale properties. In contrast, a utility investigating the root cause and possible remedial measures for TTS denting may be most

interested in TTS collar properties. Thus, in order to obtain meaningful deposit structural and compositional information, deposit samples must first be dried and separated such that the deposit types present in the as-received samples can be isolated and analyzed independently. Bulk (as-received) samples may also be analyzed for other reasons (e.g., trending sludge composition over time, evaluating impurity ingress, etc.).

Figure 3-1 summarizes typical sample preparation activities, including drying and separation, and these activities are discussed further in the sub-sections that follow. Section 3.2 summarizes the techniques used to characterize the properties of specific deposit types (i.e., segregated deposit sub-samples) after sample preparation activities are complete.

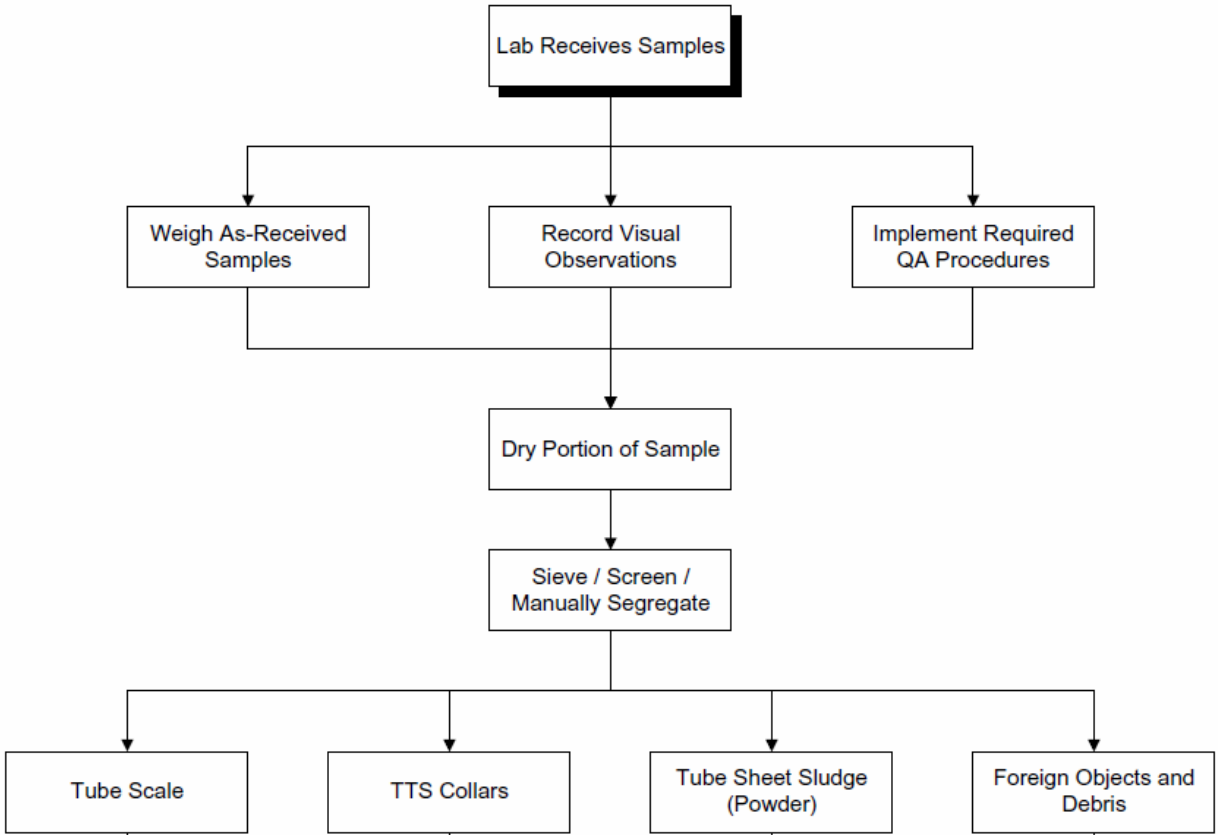

Figure 3-1
Overview of Sample Preparation Activities to Support Deposit Characterization
(adapted from Reference [1])

3.1.1. Receipt Inspection and Sample Tracking

As discussed in Section 2, deposit samples are generally obtained as wet samples in labeled bottles (see Figure 2-1 through Figure 2-3). Upon receipt of the sample or samples to be characterized, the deposit characterization personnel should visually inspect the samples to ensure that they are consistent with expectations based on documentation provided by the utility or deposit characterization personnel (e.g., sample descriptions, isotopic scans, sample masses, etc.). Appropriate quality procedures should be followed during sample preparation, and during subsequent deposit analysis, to ensure traceability of the samples throughout the characterization process.

Regardless of whether sample masses are provided with the deposit shipment, it is good practice to measure the mass of each as-received sample, and to measure the mass again after drying (discussed in the next section).

3.1.2 Drying

As noted above, many deposit types (e.g., tube scale, TTS collars, powdered sludge, foreign objects, etc.) are present in as-received deposit samples, and these deposit types must be isolated and analyzed independently to obtain deposit structural and composition information. In order to facilitate more efficient separation, the samples are generally dried prior to separation activities. It is generally recommended that samples be dried under vacuum or in an inert atmosphere at about 80°C (176°F). At these conditions, smaller samples (order 50–100 g) generally dry in 8–16 hours, whereas larger samples may require longer drying times. Temperatures over 100°C (212°F) should be avoided during the drying process to prevent the decomposition of any resin fines or beads in the sample (which may contaminate the remainder of the sample). It is generally not advisable to dry SG deposit samples in air due to the potential for conversion of typical deposit species (e.g., magnetite, copper metal, etc.) to more oxidized forms (e.g., hematite, copper oxide, etc.), which are not representative of species expected in a PWR SG. If samples are dried in air, the temperature should be maintained below 60°C (140°F) to reduce the potential for deposit oxidation.

3.1.3 Separation by Deposit Type

Once samples are dried, it is much easier to separate deposit samples into different deposit types. This is generally accomplished through a combination of sieving/screening through different size meshes (e.g., to separate powder from larger deposit pieces and debris) and manual separation (e.g., selective removal of tube scale pieces and TTS collars based on appearance and structure). Manual separation must be performed by an experienced analyst, and in some cases, deposit pieces cannot be positively categorized until they are later cross-sectioned and examined microscopically (see Section 3.2.3). The typical appearance of various deposit types (after removal from as-received deposit samples) is illustrated in Figure 3-2 through Figure 3-4, and is discussed further below:

- *Powdered Sludge*: Powdered sludge is a pulverized mixture of various deposit types and foreign material. Like other deposit types, powdered sludge is generally black in color (indicative of the deposits containing primarily magnetite), although other deposit species may also be visible macroscopically (e.g., copper). Particle sizes are generally <100 μm, and it is generally not possible to isolate the sources present within powdered sludge samples. Further, powdered sludge generally does not represent a significant percentage of the overall mass of deposits present within the SG, and may have a composition that is significantly different than SG tube scale and TTS collars.
- *Tube Scale "Flakes"*: Tube scale "flakes" are small scale pieces that formed on tubing surfaces and are found nominally intact in SG deposit samples. Typically, these flakes are scale pieces (generally on the order of a few square millimeters in surface area, although smaller and larger flakes are not uncommon) that exfoliated from tubing surfaces during prior operating cycle(s) (including during startup and shutdown) and were subsequently collected during sludge lancing. Tube scale flakes are relatively thin (generally on the order

of 100 µm) and slightly curved, with a shape consistent with these deposits having formed on the OD of SG tubing. The ID of the flake (attached to the OD of the tube) is typically smooth and glossy, while the OD of the flake (exposed to the secondary coolant) is typically rough and matte. Because tube scale generally represents a significant percentage of the overall mass of deposits present in the SGs and because tube scale properties are a primary factor that determines SG thermal performance, SG tube scale is important to examine as part of deposit characterization studies. Additionally, because tube scale flakes are found nominally intact in SG deposit samples, they facilitate an assessment of the actual composition and structure of tube scale present within the SGs. That said, it is generally not possible to determine the location at which a particular tube scale flake was formed, or to confirm that these tube scale flakes are representative of scale present on all heat transfer surfaces. As such, while average tube scale properties (e.g., thickness, porosity, etc.) can be used to estimate the overall mass of deposits present in the SGs, it is important to compare deposit loading estimates made based on average tube scale properties to those made based on other data (e.g., scale profiling, feedwater chemistry data, SG visual inspection results, etc.). Nonetheless, characterization of tube scale flakes provides valuable information for evaluating the overall condition of the SG, assessing the impact of deposits on SG thermal performance, and for preparing for and assessing the impact of potential SG maintenance activities (e.g., chemical cleaning operations) on the deposit characteristics.

- *TTS "Collars"*: Hard TTS sludge or "collars" are formed at the intersection between the SG tubing and the tubesheet, and generally larger and thicker than tube scale flakes (on the order of a few square cm in surface area). Collars are typically identified due to the fact that one face of the collar is smooth and slightly curved while a second face is smooth and relatively flat. These correspond to the surface which was attached to the tube and the tubesheet, respectively. TTS collars pieces generally have a thickness of several mm, and can cover a circumferential extent around the tube of about 10 to 45 degrees. Some particularly large collar pieces may have two curved faces, indicating that they spanned the gap between two tubes, while smaller collar pieces may be missing the flat face entirely (sometimes making it difficult to definitively identify the piece as a TTS collar). TTS collars found in deposit samples are generally pieces that exfoliated during normal operation or were removed during maintenance operations (e.g., in-bundle sludge lancing). Like tube scale flakes, TTS collars are deposit pieces that are found nominally intact in SG deposit samples, and thus a meaningful compositional and structural assessment can be made. However, it is generally not possible to determine exactly where these TTS collars formed (e.g., tube row/column), and TTS collars are also much more heterogeneous than other deposit types such that collar composition and structure can vary significantly from collar to collar. Thus, it is generally necessary to analyze a number of collars present in a given deposit sample in order to obtain a meaningful statistical distribution of properties. While TTS collars represent a relatively small percentage of the overall deposit mass, they play an important role in tubing degradation by insulating the tubes and providing an environment in which corrosion species can concentrate. Thus, characterization and monitoring of TTS collars has become increasingly important (e.g., in the context of denting assessments, and/or in support of the development of chemical cleaning processes to remove these deposits).

- *Foreign Objects and Debris*: Foreign objects and debris can consist of any number of items that have been introduced to the SGs. The most commonly identified materials are small pieces of wire, gasket pieces, and weld slag. It is important to remove these contaminants from deposit samples in order to ensure that the composition of SG deposits is accurately assessed. That said, attempts should also be made to identify foreign materials, and determine to what extent they may be contributing to SG degradation (e.g., foreign object wear, denting attributed to expansion of metallic debris, etc.).

Unless otherwise noted, analyses discussed in the remaining sections of this chapter should be performed on the specific (segregated) deposit types described above (as appropriate), and not on as-received samples, in order to obtain the most useful deposit characterization data. However, it is understood that certain deposit types (e.g., tube scale, TTS collars, etc.) may not be found in all deposit samples. In such cases, there is sometimes a need to perform analytical techniques on other available deposit types such as powdered sludge (which is generally present in all deposit samples), or on as-received samples.

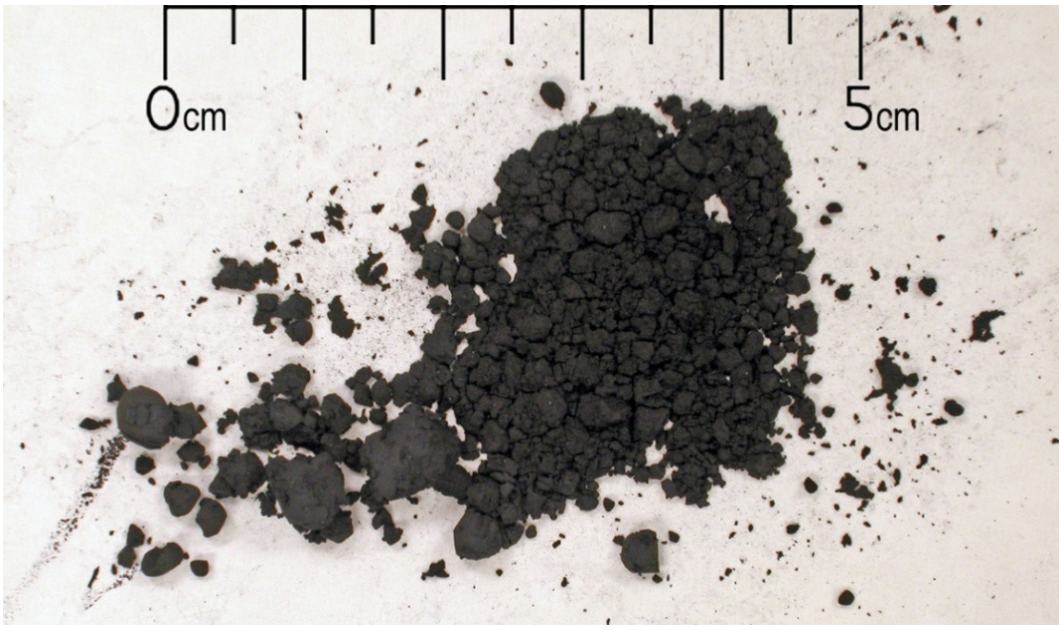

Figure 3-2
Macroscopic Photograph of Powdered SG Sludge

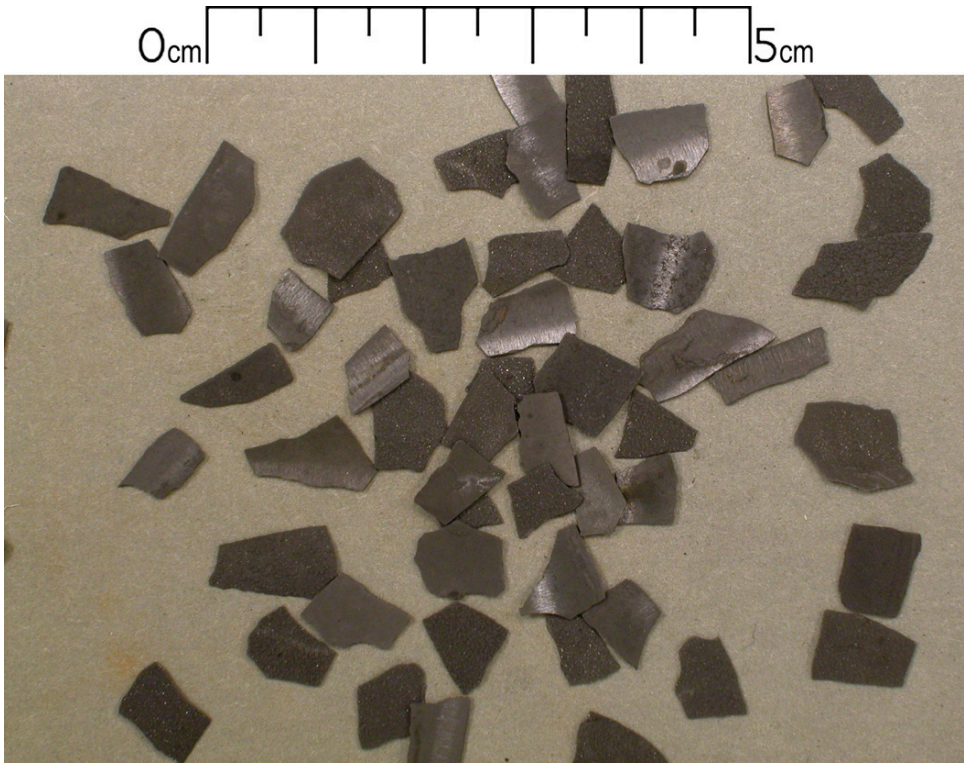

Figure 3-3
Macroscopic Photograph of SG Tube Scale "Flakes"

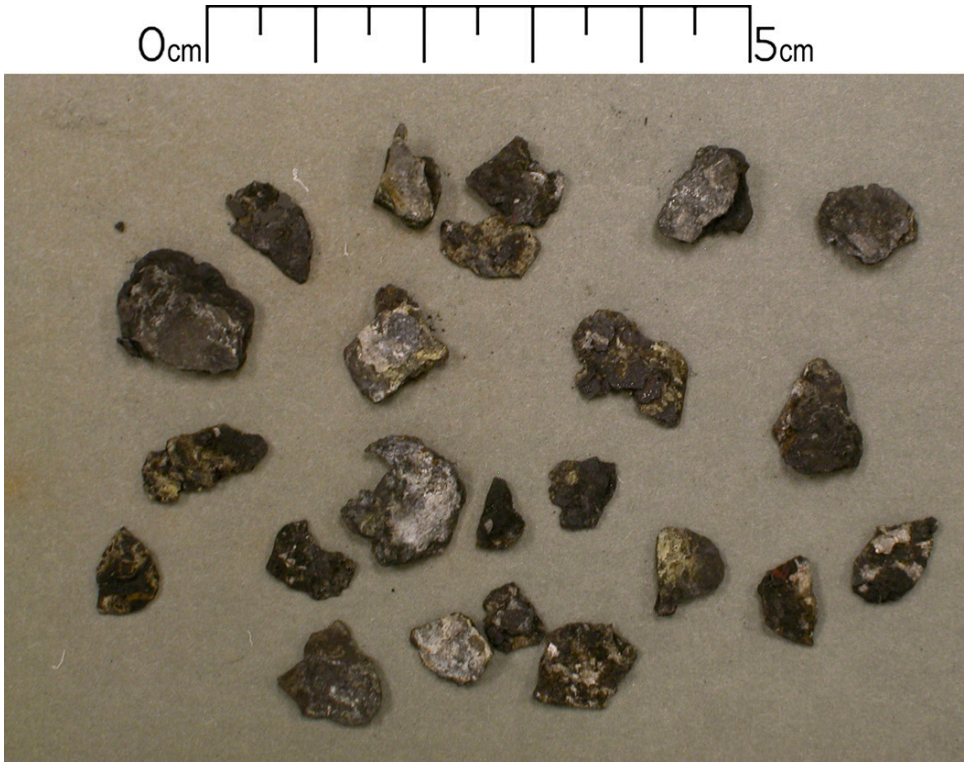

Figure 3-4
Macroscopic Photograph of TTS "Collars"

3.2 Typical Deposit Characterization Techniques

The sub-sections below describe activities that are performed during most deposit characterization studies. As discussed in Section 4, certain activities may be more or less important depending on the specific objectives, and the utility and deposit characterization vendor may agree upon the exact scope of services at their discretion.

3.2.1 Visual Observation

Visual observation of deposits allows for the characterization of macroscopic properties, including size and shape (which correlate with deposit source, as discussed above), color (which can correlate with deposit species), and general appearance. It is recommended that visual observations pertaining to both as-received samples and specific deposit types found in these samples be identified and documented via macroscopic digital photographs (with scale bars).

3.2.2 Direct Measurements

Following drying and visual observation, several techniques can be used to directly measure various properties of deposit types identified without further sample preparation. These techniques are discussed in the subsections that follow.

3.2.2.1 Dimensioning (Thickness)

Direct thickness measurements of tube scale flakes can be made using a micrometer. However, due to the curved nature of the flakes, accurately measuring the thickness may be challenging in some cases, depending on the size of each piece. Further, there may be significant variability in thickness from flake to flake. Therefore, it is recommended that a sufficient number of flake thickness measurements be obtained to ensure meaningful statistical distribution. In addition to direct measurement, tube scale flake thickness should also be measured by mounting tube scale flakes in epoxy, viewing them under a microscope in cross-section, and measuring the thickness via image analysis (see Section 3.2.3.2). Thicknesses measured directly and via image analysis should be compared to ensure consistency. When performing thickness measurements, care should be taken not to disrupt tube scale pieces.

Dimensioning of TTS collars can also provide useful information, although the irregular nature of TTS collars makes precise dimensioning difficult. Typically, TTS collars are characterized by a maximum and/or average height, base width, and circumferential extent. Similar to tube scale flakes, TTS collar dimensions can also be measured via image analysis after mounting and cross-sectioning (see Section 3.2.3.2), and thicknesses measured directly and via image analysis should be compared to ensure consistency.

3.2.2.2 Particle Size Distribution

Although not necessarily reflective of the particle size distribution (PSD) of deposits present within the SG, the PSD of an as-received deposit sample may be estimated by passing the sample through mesh sieves of various sizes. The mass of deposits retained and passed through each size mesh can then be used to quantify the percentage within a given size range (e.g., <40 μm,

40 – 100 µm, 100 µm – 1 mm, >1 mm). As noted above, this type of sieving also helps to begin the process of separating as-received deposit samples into different deposit types since tube scale flakes and TTS collars tends to remain with larger particle sub-samples, while powdered sludge tends to concentrate in smaller particle sub-samples (see Section 3.1.3).

If desired, more detailed PSD analysis may be performed using particle size analyzers, laser diffraction (Mie scattering), and electrical sensing (Coulter counting). Additionally, computer-assisted image analysis of optical photomicrographs may be used to determine particle size distributions.

3.2.3 Microscopic Analyses

3.2.3.1 Cross-Sectioning

Following direct visual examination, it is recommended that tube scale flakes and TTS collars be mounted in epoxy (e.g., conductive Bakelite) and examined in cross-section using standard metallographic techniques. Examining the cross section of deposits can provide useful information regarding thickness, internal structure (e.g., porosity), and composition, as discussed in the sub-sections that follow. Further, examining deposit pieces in cross-section serves to verify the deposit type. (As noted above, in some cases deposit pieces may resemble SG tube scale macroscopically, but are later determined not to be tube scale based on examination of the deposit structure in cross-section at high magnification.) An example photograph showing TTS collars mounted in epoxy and polished in preparation for cross-sectional examination is shown in Figure 3-5. As shown in this figure, markers are often added to mounts so that separate documentation can relate the location of the marker to the identification of various specimens in the same mount. Markers may also be used to document the location of various deposit surfaces (e.g., tube OD, tube ID, and tubesheet surface).

The number of tube scale flakes and TTS collars to be examined depends on a number of considerations. For example, the number of TTS collars present in a SG deposit sample is typically relatively small and these deposit pieces may be needed for other activities such as SG chemical cleaning qualification testing. Thus, a utility or deposit characterization vendor may decide to limit the number of TTS collars to be destructively examined by cross-sectioning during a deposit characterization study. On the other hand, cross-sectioning and examining these deposit pieces provides valuable information that could be used to optimize the SG chemical cleaning process. The same basic trade-offs apply for tube scale flakes, and in many cases, the number of tube scale flakes examined is a compromise between the expected value of the information through cross-section and the mass of material needed for other analyses and related activities.

It is worth noting that in some cases, the quantity of tube scale or TTS collars present in a deposit sample is very limited. In such cases, it is common to make best efforts to perform the most useful deposit characterization activities such as destructive examination by cross-sectioning, elemental analysis by ICP techniques such as ICP-OES and/or ICP-MS, etc., and to use this information to select a surrogate plant deposit or to develop appropriate deposit simulants (with chemical and physical properties that match the SG deposit of interest) for use during other activities such as SG chemical cleaning qualification testing.

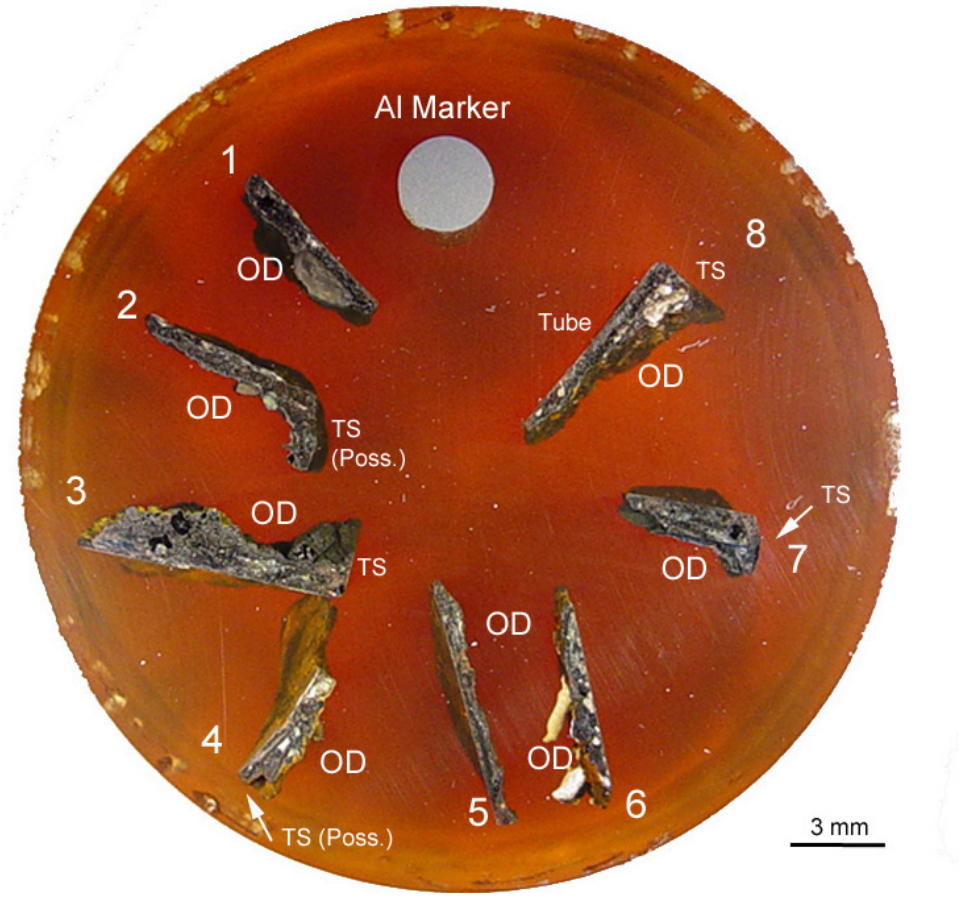

Figure 3-5
TTS Collars Mounted in Epoxy and Polished to Reveal Cross-Sectional Structure

3.2.3.2 Optical Microscopy and Image Analysis

After tube scale flakes and TTS collars are mounted in cross-section and polished (as illustrated in Figure 3-5), optical microscopy is typically used to examine the composition and structure of these deposit types. Typically, magnification in the range of 50–500X is appropriate for examining structural deposit features and observations should be documented in digital images with scale bars. Both bright field and dark field lighting should be used when examining TTS collars. Bright field lighting highlights normal color differences, for example, highlighting copper inclusions. Dark field lighting highlights optically active constituents, including, for example, silica. Bright field lighting is generally appropriate for examining tube scale flakes since the primary species of interest are magnetite and metallic copper, and lower concentrations of other species are typically present.

Generally, optical microphotographs should be used to document the entire cross-section of any TTS collars that are mounted and cross-sectioned. Within the recommended magnification range, multiple microphotographs must generally be taken and combined to generate a single, high resolution image showing the entire collar cross-section. Figure 3-6 shows example high magnification photomicrographs of a TTS collar shown in bright field and dark field lighting. The individual high-magnification images have been merged to provide a complete image of the collar, then reduced in size to fit into this report.

Because the structure of tube scale flakes is generally much more homogeneous than that of TTS collars, it is not necessary to document the entire length of each flake cross-section (as is recommended for TTS collars). However, a representative microphotograph is generally taken for each tube scale flake that is examined. The photograph is generally taken at a location that is representative of the properties (e.g., thickness, porosity, copper content and distribution, etc.) along the remaining length of the tube scale flake when viewed in cross-section. Within the recommended magnification range, the cross-sectional thickness of each tube scale flake can generally be documented in a single microphotograph. Figure 3-7 shows example high magnification photomicrographs of two tube scale flakes, both shown in bright field lighting. The number of tube scale flakes to be examined as part of a deposit characterization study depends on a number of factors (as discussed above). However, it is generally advisable to examine a sufficient number of tube scale flakes to quantify statistical variations in deposit properties.

Once digital microphotographs have been compiled as described above, the general appearance of various deposit pieces should be reviewed to guide the remainder of characterization activities. For example, points of interest such as metallic inclusions or obvious changes in composition should be identified for subsequent analyses such as SEM/EDS (to confirm composition) or microhardness measurements (to confirm hardness at specific locations). Further, experienced analysts may also be able to make qualitative compositional estimates (e.g., approximate copper content), and these expectations may be compared to later quantitative analyses (e.g., by ICP). Finally, image analysis software should be utilized to assess the porosity and thickness of each deposit piece that is examined. As noted above, a sufficient number of deposit pieces should be examined by image analysis to obtain meaningful statistical information. Note that if a tube scale flake or collar piece is mounted at an angle (i.e., if the circumferential direction is not normal to the mount surface), it will cause the flake or collar thickness measurement to be biased high.

The following general comments and observations are made in regard to examination of tube scale and TTS collars by optical microscopy and image analysis:

- The composition of SG tube scale is generally homogeneous, although there may be slight compositional variations along the thickness of the tube scale (e.g., nickel may be present at higher concentration near the ID surface of the tube scale). The structure of tube scale is somewhat porous, and the porosity may vary along the thickness of the tube scale. Copper inclusions, when present, are typically metallic inclusions distributed within the magnetite-based scale matrix as can be seen in Figure 3-7. The composition of TTS collars is typically much more heterogeneous than tube scale (with higher concentrations of deposit species such as aluminosilicates), and the structure of TTS collars is typically very dense (little to no porosity) as can be seen in Figure 3-6 .
- Thickness measurements obtained using image analysis should be compared to those obtained by direct measurement to ensure consistency.
- Porosity as measured by image analysis should be compared to porosity of deposit pieces measured using pycnometry techniques (see Section 3.3.3). In general, porosity measurements obtained by image analysis are preferred, particularly when tube scale has been exposed to soft cleaning techniques. Soft cleanings can lead to large pore sizes, particularly near the exterior of scale pieces, which can lead to inaccuracies when measuring

the porosity using pycnometry techniques. In contrast, when image analysis is used to measure porosity, the area of interest can be cropped at the discretion of the analyst and the porosity can be measured in very specific locations (e.g., with edge effects excluded, within specific sub-layers or over the entire cross-section). This capability is very beneficial, particularly when deposit characterization activities are being performed in support of heat transfer studies (e.g., to assess structural changes resulting from a soft cleaning, as part of a thermal performance evaluation, etc.).

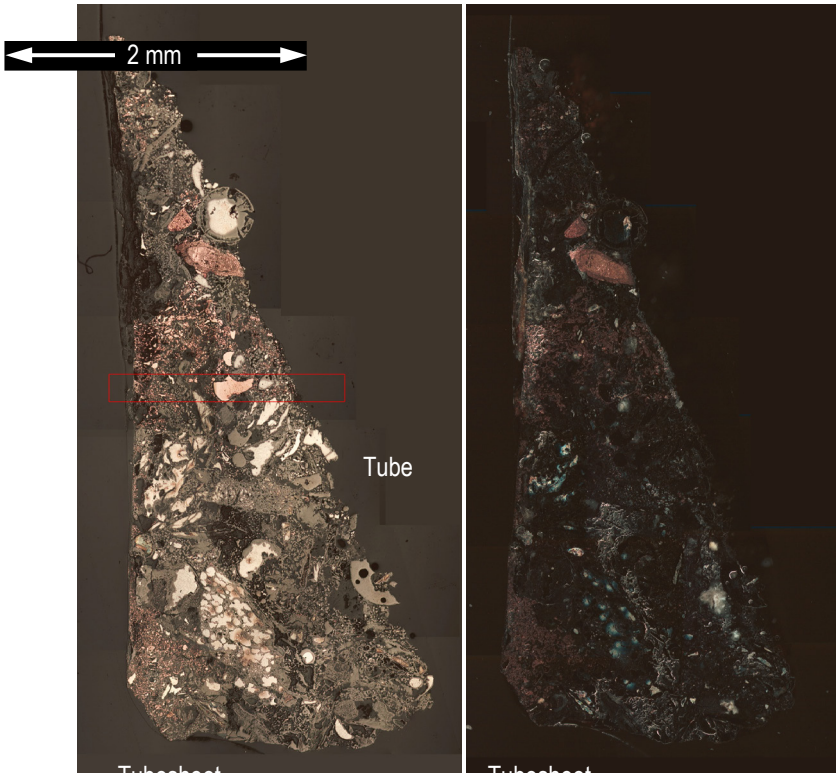

Figure 3-6
TTS Collar Viewed in Cross-Section at High Magnification with Bright Field Lighting (left) and Dark Field Lighting (right)

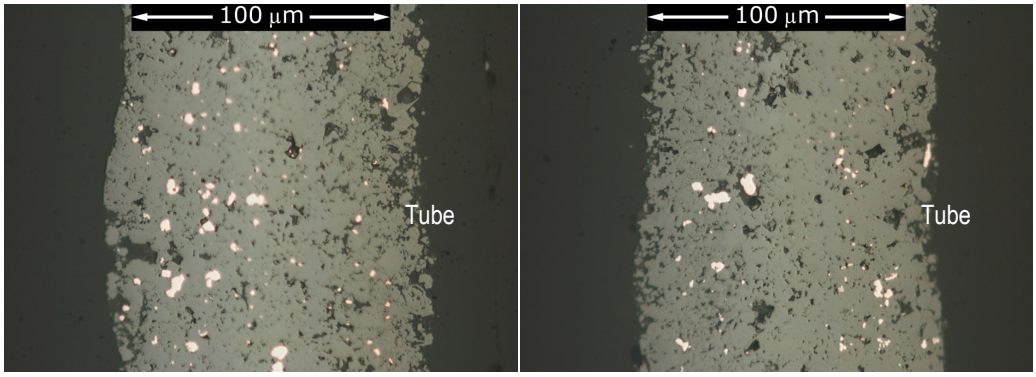

Figure 3-7
SG Tube Scale Viewed in Cross-Section at High Magnification (Bright Field Lighting)

3.2.3.3 Scanning Electron Microscopy / Energy Dispersive Spectroscopy (SEM/EDS)

Scanning electron microscopy (SEM) can be used to examine tube scale flakes and TTS collars that have been mounted in epoxy and cross-sectioned in the same way as described in the previous section for optical microscopy. The two techniques are complimentary in that optical microscopy is useful for obtaining most of the desired cross-sectional images and SEM may be beneficial for examining points of interest at much higher levels of magnification and for obtaining local compositional information at these points using energy dispersive spectroscopy (EDS). Example images and data illustrating the identification and examination of local points of interest using SEM/EDS are shown in Figure 3-9 through Figure 3-11 and Table 3-1. (For comparison, Figure 3-8 shows an optical microphotograph of the same SEM microphotograph shown in Figure 3-9.) Note that the example TTS collar shown in these figures is the same TTS collar shown in full cross-section in Figure 3-6 (the "region of interest" is highlighted using a red box). The following observations are made regarding these figures:

- Figure 3-8 shows optical microphotographs of the region of interest within a TTS collar using bright and dark field lighting. As opposed to SEM micrographs, optical microscopy provides color and transparency information which can be used to infer information regarding phase identification. For example, a large copper inclusion can be seen near the center of the TTS collar shown in Figure 3-8.
- Figure 3-9 shows secondary and backscattered electron SEM images of the same areas as Figure 3-8. Secondary electron imaging is advantageous for revealing surface topography such as the microhardness indentations. As mentioned above, contrast in backscattered electron images depends on atomic number. In Figure 3-9, the brightness of the interior of a particle is indicative of a metallic phase.
- Figure 3-10 shows thirteen points at which EDS point spectra and microhardness measurements were obtained. The elemental composition information obtained by EDS at these locations is summarized in Table 3-1. EDS results summarized in Table 3-1 show, for example, that inclusions located at points #4, #5 and #11 are metallic copper, stainless steel and carbon steel, respectively. The presence of carbon steel at point #11 is further confirmed by the presence of oxidation (corrosion) around this inclusion (see annular region encompassing point #11 in Figure 3-10). EDS analysis taken at point #12 within this annular region confirm that this is an iron oxide layer formed on the carbon steel inclusion located at

point #11 (see Table 3-1). As discussed in other industry references, corrosion of carbon steel or low alloy steel particles embedded within hard TTS sludge or corrosion of the underlying tubesheet results in volumetric expansion of these metallic substrates, which can lead to tube denting [4, 6]. Microhardness is discussed further in Section 3.2.3.4, and the microhardness measurements taken at the thirteen locations shown in Figure 3-10 are summarized in Table 3-2.

- Figure 3-11 shows an EDS elemental map of the left side of the collar shown in Figure 3-9. As shown in this figure, the collar is comprised of a matrix of magnetite with dispersed aluminosilicates and copper inclusions.

Unmounted tube scale flakes and TTS collars can also be examined by SEM/EDS. This allows all surfaces of a specimen (ID, OD, and cross-section) to be characterized. The cross-sectional surface examined should be a "fresh break" generated in the laboratory by fracturing the as-received specimen, whenever permitted by specimen geometry. While the precision and accuracy of EDS elemental analyses may be slightly compromised relative to examining a polished surface, the morphology of features such as crystalline structures and pores/steam chimneys (especially on the cross-section and OD surfaces) can be examined in greater detail. Belt polishing marks or other features from tube manufacturing may also be visible on the ID of the tube scale. Example images and data illustrating the examination of unmounted specimens are shown in Figure 3-12 through Figure 3-14.

SEM is a technique for generating an image of a sample (mounted or un-mounted) by bombarding the sample with a focused beam of high energy electrons in a raster pattern and collecting the electrons which are generated or reflected. Electrons which are generated when the beam interacts with the sample surface are called secondary electrons and provide contrast according to the surface topography of the specimen (among other factors), which is what enables the generation of an image. In addition to secondary electrons, backscattered electrons (BSE), electrons from the original beam which have been reflected back by the atoms in the sample, can also be collected to form an image. As elements with larger nuclei are more likely to reflect electrons, the contrast in an image generated using backscattered electrons shows compositional differences. Depending on the exact arrangement of the detector, backscattered electrons can also be used to generate images based on topographical differences. Additionally, a specialized detector for measuring the diffraction of backscattered electrons can be used to measure the crystallographic structure of materials. This technique is known as electron backscatter diffraction (EBSD) or backscatter Kikuchi diffraction (BKD). Finally, it should be noted that SEM and other electron bombardment techniques typically require an electrically conductive sample, while deposits mounted in epoxy are generally non-conductive. It is therefore necessary to sputter-coat mounted samples with a thin layer of carbon (or other conductive material such as gold) prior to analysis. While a conductive sample is needed to provide the highest resolution images for a conventional sample, it is noted that many modern SEMs are capable of imaging completely non-conductive samples, by injecting a small amount of nitrogen or argon in the sample chamber which in turn ionize and help neutralize the surface charge generated by the impingement of the electron beam on the non-conductive sample.

As noted above, SEM-EDS is a technique for measuring elemental composition at very specific locations. As noted above, this is typically performed on deposit cross-section after mounting in epoxy and polishing, but may also be performed directly on unmounted deposit pieces. When a secondary electron is ejected from the electron cloud of an atom in the sample, an electron from a higher energy orbital will fill the lower energy electron hole, emitting an X-ray with an energy characteristic of the energy transition in the process. EDS is the process of measuring the number and energy of these X-rays to determine the composition of a sample. As electrons accelerated with typical beam energies (e.g., 5-30 keV) will interact with deposit materials to a characteristic depth on the order 1 μm (0.04 mil) [24], SEM-EDS can generally be used to semi-quantitatively measure the composition of features of interest identified by SEM or optical microscopy. Lower beam energies reduce the size of the interaction volume at the expense of lower count rates, while higher beam energies increase the rate of X-ray generation and thus the rate of data collection at the expense of lower EDS spatial resolution. EDS can readily detect species present at concentrations of 0.5 wt% or greater, and can often detect lower concentrations. EDS cannot detect the light elements hydrogen, helium, or lithium because they do not have occupied higher energy orbitals [24]. For the same reason, quantitative correction coefficients associated with lower atomic number species (i.e., carbon and lighter elements) are very large and can negatively impact accuracies.

As discussed above, EDS is typically performed at specific points of interest to identify the composition of a specific feature within a deposit piece. However, EDS can also be performed over a larger area to obtain the average composition within that area. The analysis location or area should always be reported along with the EDS compositional results such that these results may be interpreted in this context (i.e., as the composition of a specific inclusion within the deposit matrix, or as a semi-quantitative average composition taken over a larger area). EDS accuracy is dependent on X-ray attenuation and therefore depends on what elements are being examined, as well as the sample homogeneity, but EDS analysis results typically have an accuracy of about ±10% for light elements and about ±1% for transition metals such as iron and nickel.

A related technique that is worth mentioning is scanning electron microscopy - wavelength dispersive spectroscopy (SEM-WDS). SEM-WDS is similar to SEM-EDS, with the exception that the wavelength of the emitted X-rays is measured rather than the energy. An SEM-WDS detector can only measure the concentration of one element (one wavelength) at a time. However, the spectral resolution achieved with WDS is better than with EDS (i.e., decreased peak width), resulting in more precise quantification of elemental compositions. WDS is also more sensitive than EDS, often detecting elemental concentration down to tens of ppm, including light elements, which are more problematic for EDS. WDS is often collected at much higher beam currents. Although this improves detection sensitivity, it also degrades spatial resolution of the analysis. Because SEM-EDS is less labor intensive (multiple elements can be analyzed simultaneously) and is generally effective for obtaining local compositional information within SG deposits, SEM-EDS is more commonly used during deposit characterization studies.

Table 3-1
Summary of SEM/EDS Point Spectra Taken at Points of Interest

Measurement Number		#1	#2	#3	#4	#5	#6	#7	#8	#9	#10	#11	#12	#13
Element Normalized Wt % (Carbon Excluded from Normalization)	Nitrogen	-	-	-	-	-	-	-	-	-	-	-	-	-
	Oxygen	75.4	42.0	31.8	1.3	-	32.4	55.8	-	0.8	1.1	-	29.9	0.7
	Fluorine	-	-	-	-	-	-	-	-	-	-	-	-	-
	Sodium	-	0.9	-	-	-	-	-	-	-	-	-	-	-
	Magnesium	-	1.0	-	-	-	-	-	-	-	-	-	-	-
	Aluminium	-	14.9	-	-	-	-	43.7	-	-	-	-	-	-
	Silicon	-	4.9	-	-	-	-	-	2.4	-	-	-	-	-
	Phosphorus	-	-	-	-	-	-	-	-	-	-	-	-	-
	Sulfur	-	-	-	-	-	-	-	-	-	-	-	-	-
	Chlorine	19.0	-	-	-	-	-	-	-	-	-	-	-	-
	Potassium	-	-	-	-	-	-	-	-	-	-	-	-	-
	Calcium	-	-	-	-	-	-	-	-	-	-	-	-	-
	Scandium	-	-	-	-	-	-	-	-	-	-	-	-	-
	Titanium	-	-	-	-	-	-	-	-	-	-	-	-	-
	Vanadium	-	-	-	-	-	-	-	-	-	-	-	-	-
	Chromium	-	-	-	-	18.8	-	-	-	-	-	-	-	19.1
	Manganese	-	1.1	-	-	-	-	-	-	1.2	1.0	-	-	1.7
	Iron	5.6	34.2	66.4	2.7	72.2	67.6	0.5	95.1	1.5	1.4	100.0	70.1	69.5
	Cobalt	-	-	-	-	-	-	-	-	-	-	-	-	-
	Nickel	-	0.9	1.8	-	9.0	-	-	2.5	9.8	9.2	-	-	9.1
	Copper	-	-	-	96.0	-	-	-	-	86.7	87.3	-	-	-
	Zinc	-	-	-	-	-	-	-	-	-	-	-	-	-
	Arsenic	-	-	-	-	-	-	-	-	-	-	-	-	-
	Zirconium	-	-	-	-	-	-	-	-	-	-	-	-	-
	Niobium	-	-	-	-	-	-	-	-	-	-	-	-	-
	Molybdenum	-	-	-	-	-	-	-	-	-	-	-	-	-
	Silver	-	-	-	-	-	-	-	-	-	-	-	-	-
	Tin	-	-	-	-	-	-	-	-	-	-	-	-	-
	Barium	-	-	-	-	-	-	-	-	-	-	-	-	-
	Tungsten	-	-	-	-	-	-	-	-	-	-	-	-	-
	Lead	-	-	-	-	-	-	-	-	-	-	-	-	-

a) Left to Right ≈ Increasing Distance from Tube Surface.

b) Measurement #1 was collected on the mounting epoxy.

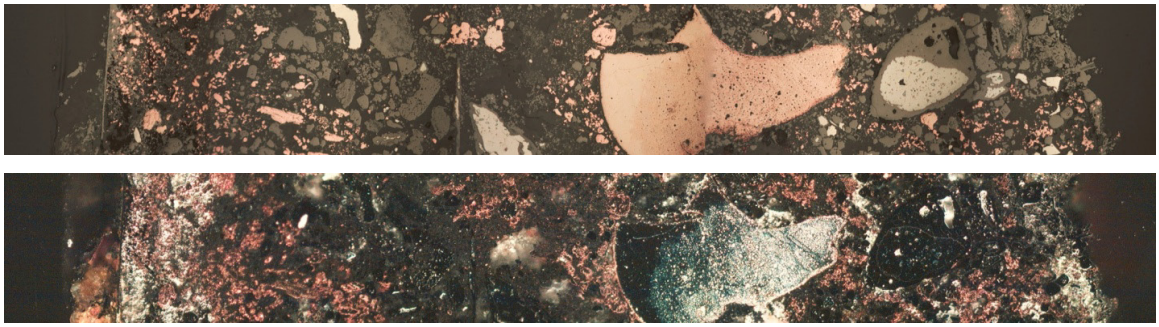

Figure 3-8
Optical Microphotograph of Region of Interest within TTS Collar (Top: Bright Field Lighting/Bottom: Dark Field Lighting)

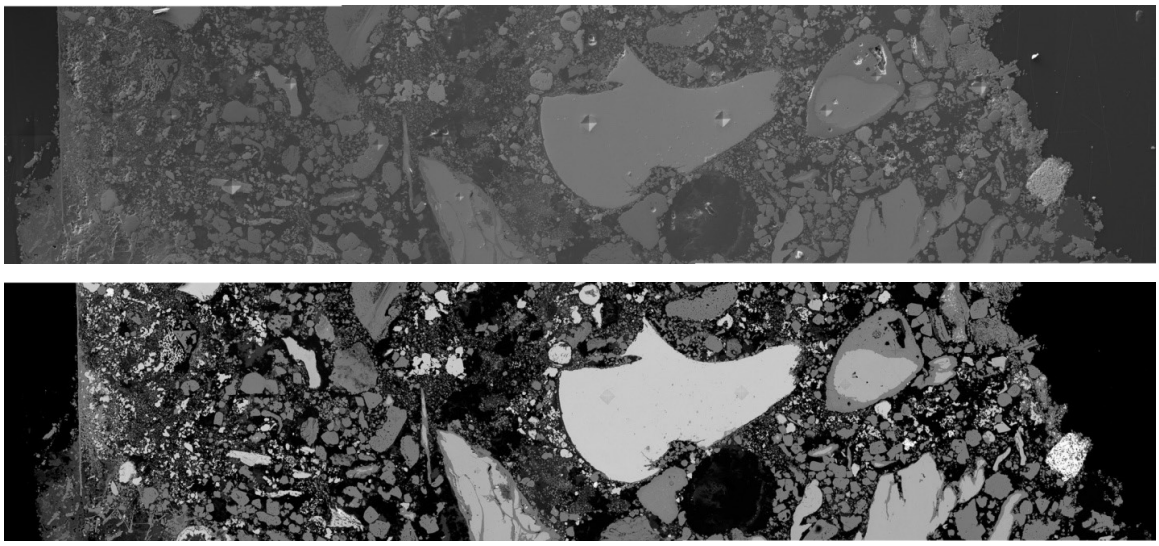

Figure 3-9
SEM Microphotograph of Region of Interest Within TTS Collar (Top: Secondary Electron Detector/Bottom: Backscatter Detector)

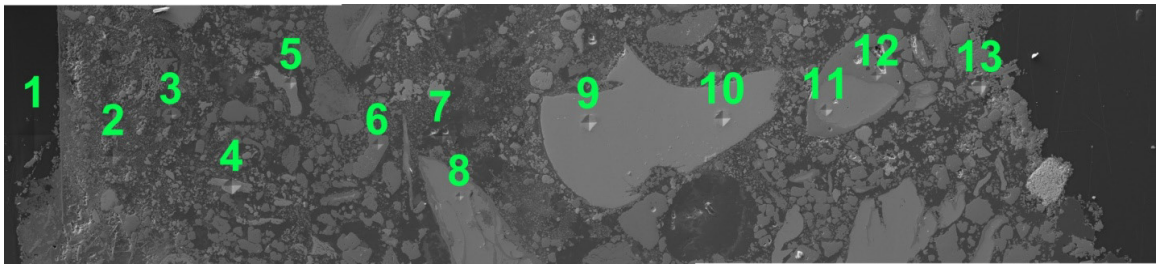

Figure 3-10
Points of Interest Identified within TTS Collar

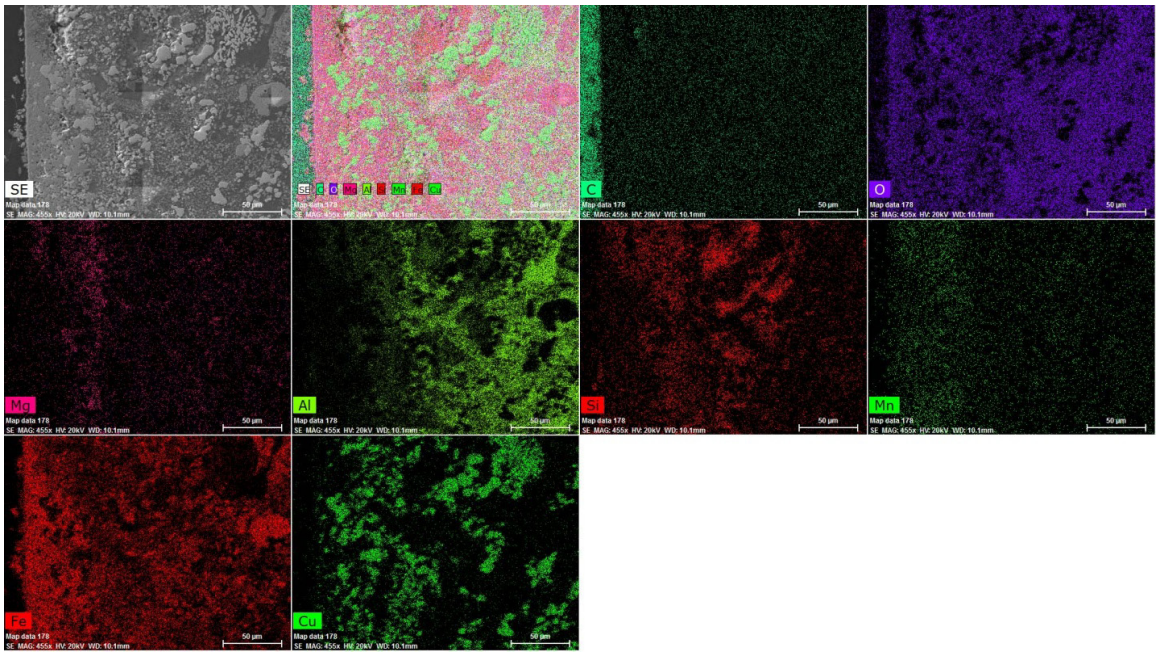

Figure 3-11
SEM/EDS Compositional Map Taken at Left Side of Region of Interest

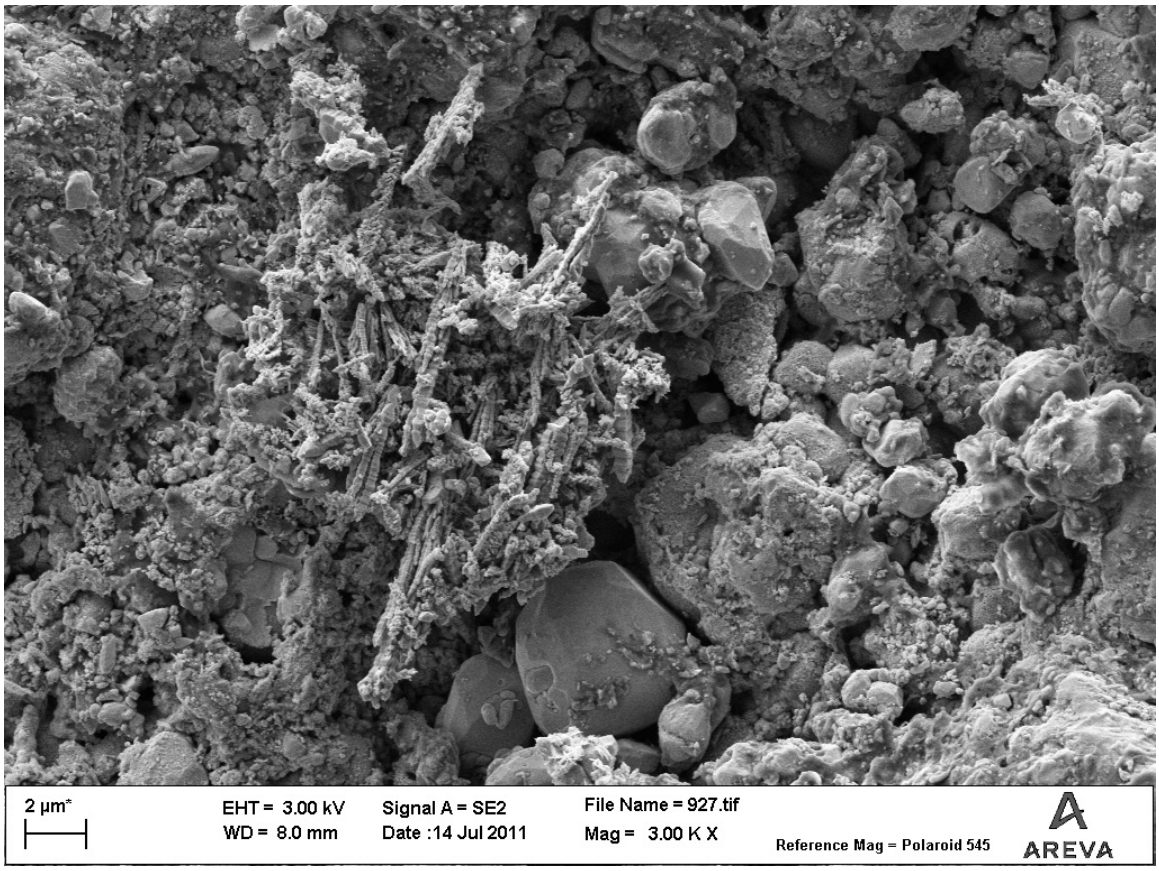

Figure 3-12
SEM Micrograph of Scale OD Showing Steam Chimney Openings and Titanium-Rich Crystals Just Left of Center (Secondary Electron Detector)

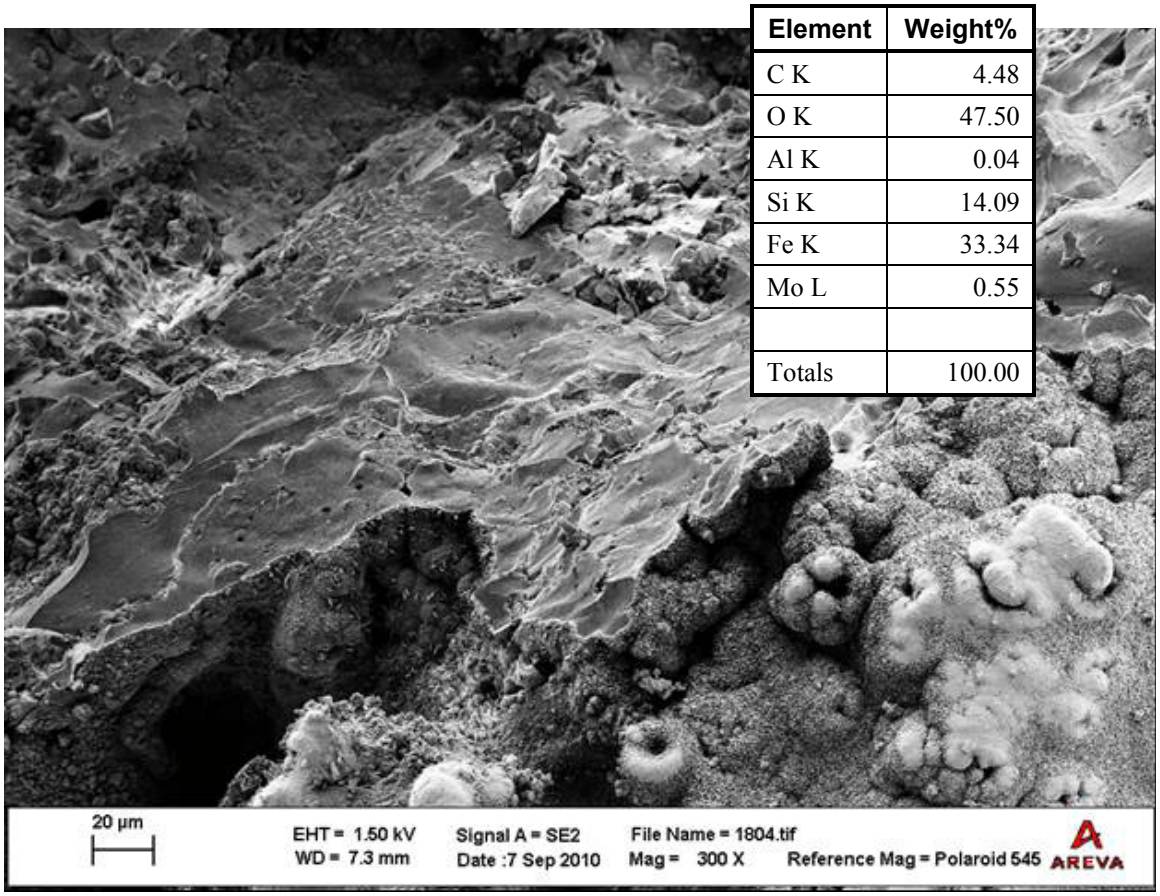

Figure 3-13
SEM Micrograph and EDS Composition Data of Collar Cross-Section Area Exhibiting Nodular Formations in Lower Right of Image (Secondary Electron Detector)

Figure 3-14
Higher Magnification SEM Micrograph and EDS Composition Data of Nodular Formations in Figure 3-13 (In-Lens Secondary Electron Detector[2])

3.2.3.4 Microhardness

In the same way that SEM/EDS is typically performed on deposit cross-sections to obtain local composition information at specific points of interest, microhardness measurements are also typically performed on these cross-sectional faces to obtain physical data at specific points of interest. Since these measurements are primarily dependent on the local composition at the measurement location, microhardness measurements are generally performed only for TTS collars, which have a more heterogeneous composition. However, they may optionally be performed on other deposit types (e.g., tube scale) or on foreign objects found in deposit samples. Example microhardness measurements taken at the points of interest along the cross-section of the example TTS collar shown in Figure 3-10 are summarized in Table 3-2. The locations at which microhardness measurements were taken are visible as diamond-shaped indentations in Figure 3-10.

[2] An in-lens secondary detector filters out more backscatter than a "standard" secondary detector and provides better morphology imaging.

Microhardness measurements are similar to macrohardness measurements (see Section 3.3.1) in that they provide information on the mechanical strength of the material being tested. However, microhardness measurements are obtained at very specific locations, and facilitate measurement of mechanical strength at many different locations within the deposit matrix (e.g., along the thickness of a TTS collar, from the tube surface to the collar outer surface). Microhardness is most commonly measured by applying a known force to a diamond indenter of known geometry to create an indent in the material of interest. The size of the indent is then measured under an optical microscope. Microhardness is typically reported with units of kgf/mm^2 and is calculated as the ratio of the force applied to the indent size, with a factor for the geometry of the indenter. The geometry of the indenter depends on the specific microhardness technique being used (Vickers and Knoop indenters are two of the most common) and can affect the numerical result. Therefore, it is important to consider the measurement technique used when evaluating microhardness data. Typical Vickers microhardness measurements have a diagonal length on the order of 25 µm (1 mil), which is small enough that the hardness values of individual compositional inclusions in deposits (e.g., copper, aluminosilicates, metallic fragments embedded within the deposit structure, etc.) can often be measured.

As with macrohardness measurements, microhardness measurements provide information on relative deposit strengths, aid in the development of realistic deposit simulants, and may inform decisions regarding mechanical cleaning techniques [25, 26].

Table 3-2
Summary of Microhardness Measurements Taken at Points of Interest

Position	Vickers Pyramid Number (HV)
1[a]	19.8
2[b]	121.6
3	427.8
4	157.8
5	266.3
6	382.4
7	139.6
8	646.0
9	185.2
10	196.8
11	321.7
12	432.9
13	158.7

a) Measurement collected on collar mount epoxy.
b) Two indentation made; HV only recorded for lower point.

3.2.4 Bulk Analyses

Bulk analyses are analyses performed on a small sample of deposits or on an entire deposit piece to measure the average properties within the entire sample or entire deposit piece. Bulk analyses are typically used to determine the average composition of specific deposit types found in deposit samples (e.g., SG tube scale, TTS collars, powdered sludge, etc.), which is a key characteristic that is important for understanding how deposit may impact material integrity or thermal performance, and/or for developing chemical cleaning processes to remove these deposits. Typically, bulk analyses are performed on a small sample of tube scale flakes or on an individual TTS collar. However, bulk analyses may also be performed on as-received deposit samples, powdered sludge sub-samples, or foreign objects / debris.

Bulk analyses are generally performed separately on deposit types of interest found in any of the as-received deposit samples (e.g., one analysis each for tube scale flakes found in samples from SG-A, SG-B and SG-C). However, bulk analyses are destructive in that deposits must be pulverized, and in the case of ICP techniques – dissolved in acid, in order to facilitate compositional analysis. As such, if limited deposit quantities are available, quantities required for other analyses and related activities (e.g., cross-sectioning, SG chemical cleaning qualification testing, etc.) should be considered when determining how many bulk analyses should be performed, and with which specific samples or deposit types.

3.2.4.1 Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) and Mass Spectrometry (ICP-MS)

Compositional analysis of SG deposit samples is an important activity for any deposit characterization, and inductively coupled plasma optical emission spectrometry (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS) are the most common techniques used for measuring the elemental composition of deposit samples. These techniques can be used to accurately analyze for many different elements simultaneously, and deposit samples are typically analyzed for the following set of elements (at a minimum): Fe, Cu, Zn, Ni, Si, Ca, Mn, Al, Ti, Cr, P, Mg, Co, and Pb. ICP-OES is also referred to as inductively coupled plasma atomic emission spectroscopy (ICP-AES).

Both ICP-OES and ICP-MS rely on the analysis of liquid samples. Thus, solid deposit samples of interest must first be dissolved in an acid matrix to facilitate analysis by these techniques. This is typically accomplished by first grinding a portion of the sample into a uniform fine powder. A known (small) mass of this powder is then dissolved in a strong acid (or mixture of strong acids) and the resulting solution is diluted to a known volume prior to measurement to protect the ICP equipment. (Dilution factors are later used to calculate the elemental concentrations present in the initial deposit sample.) After these liquid solutions are prepared, ICP is performed by passing the liquid through a nebulizer (to create a mist) into a plasma (typically argon), which breaks apart and ionizes the molecules and elements present. For ICP-OES, an optical spectrometer is then used to measure the intensities of characteristic wavelengths of light given off by different elements. The relative intensities can be converted to concentrations via measurement of a standard with a known composition. For ICP-MS, a mass spectrometer is used to measure the mass-to-charge ratio of the ions generated in the plasma. The specific mass-to-charge ratios measured and the frequency of their measurement allows for the calculation of the species present in the original sample.

Following analysis to determine the concentration of the different elements present in the deposit samples, assumed oxide forms (based on prior experience or information from other analytical techniques such as X-ray diffraction or Mössbauer spectroscopy) can be used to back calculate the mass of the various phases present in the original sample that was dissolved. If the calculated mass is found to be substantially lower than the original mass, then the analysis should be reviewed to determine if any elements were missed or if incomplete dissolution of the sample may have occurred. If the calculated mass is found to be substantially higher than the original mass, the assumed oxides selected should be reviewed. Assumed compounds typically used for this intermediate mass balance are as follows (for the matrix of elements identified above): Fe_3O_4, Cu, $Fe_{3-x}Zn_xO_4$, $Fe_{3-x}Ni_xO_4$, SiO_2, $CaSO_4$, $Fe_{3-x}Mn_xO_4$, AlOOH, $Fe_{3-2x}Ti_xO_4$, $Fe_{3-x}Cr_xO_4$, Na_2HPO_4, $MgSO_4$, Co_2O_3, and PbO. The actual compound forms present are later confirmed using X-ray diffraction (see Section 3.2.4.2).

Although less common than ICP, several other elemental analysis techniques are available and worth mentioning, including:

- *Direct coupled plasma optical emission spectrometry (DCP-OES) and direct coupled plasma mass spectrometry (DCP-MS)*: These techniques are similar to ICP-OES, but utilize a slightly different plasma configuration.
- *Atomic absorption spectroscopy (AAS)*: In AAS, deposits dissolved in a liquid are first atomized, typically by passing the sample into a flame or a graphite furnace. The atomized sample is then exposed to a light source. The absorption of a wavelength of light characteristic to an element is measured and can be correlated to a concentration of that element through the use of standard solutions of known concentration. AAS is only capable of analyzing one element at a time.

3.2.4.2 X-Ray Diffraction (XRD)

X-ray diffraction (XRD) is a bulk analysis technique that is complementary to ICP. In the same way that ICP is typically used to analyze the elemental concentrations of species present in SG deposit samples (Fe, Cu, etc.), XRD is typically used to determine the compound forms of these species (magnetite, versus metallic iron, for example).

XRD is an analytical technique for determining the structure of crystalline materials by X-ray bombardment from a known source. The incident X-rays are diffracted at by various crystallographic planes of atoms in crystallites of the sample. If the diffracted X-rays at a given angle constructively interfere, the diffraction is strong enough for these X-rays to be measured by a detector, which measures the intensity of the diffraction and the angle where the diffraction took place. Therefore, the series of angles at which constructive interference occurs during a scan of a sample can typically be used to identify the compound or compounds which make up a sample. XRD is typically performed on powdered samples. Thus, deposit samples to be analyzed (e.g., a sample of tube scale flakes, an individual TTS collar, etc.) are generally pulverized prior to analysis by XRD.

X-ray diffraction is particularly useful for distinguishing compounds which have similar chemical formulas, but different structures (such as magnetite and hematite). However, it is not always capable of distinguishing compounds which have the same crystallographic structure and similar lattice spacings (such as magnetite, nickel ferrite, and other substituted spinels). Nonetheless, if a sample is known to contain both iron and nickel and only a spinel structure is detected by XRD, it can then be inferred that the nickel is present as nickel ferrite. Lower detection limits vary for XRD, but are typically on the order of 5 wt%.

3.3 Other Deposit Characterization Techniques

Numerous additional analytical techniques exist which can aid in the characterization of SG deposits. Although less commonly used than the techniques described above, the techniques described in this section can provide valuable information in certain circumstances and may be considered based on the specific objectives of a deposit characterization program.

3.3.1 Macrohardness / Crush Strength

Macrohardness measurements are not routinely included in the scope of all deposit characterization studies because they result in the destruction of the deposit piece in question (e.g., a TTS collar), and because they may not always be required. That said, in some cases (e.g., if a utility is preparing for a mechanical cleaning operation to remove TTS collars), the information obtained by macrohardness measurements may be useful and therefore these measurements may be considered. It is worth noting that microhardness measurements (discussed in Section 3.2.3.4) are generally performed in lieu of macrohardness measurements because deposits are already cross-sectioned as part of most deposit characterization studies, and microhardness measurements can be performed on the cross-sectional faces of deposit pieces of interest (e.g., TTS collar) without the need to destructively examine additional deposit pieces that are found intact in SG deposit samples.

Macrohardness measurements (also referred to as crush strength measurements) provide information on the mechanical strength of the deposit material by direct measurement of the amount of force required to break a deposit piece. The force required is typically applied by squeezing the sample between a movable conical probe or flat plate attached to a force gauge and a fixed flat plate. Macrohardness measurements can be performed using constrained or unconstrained testing. In constrained testing, the sample is bounded on all sides by the test apparatus, while in unconstrained testing the specimen is free to expand outwards as force is applied. The entire substrate must fail during constrained testing. In contrast, during unconstrained testing, a single fault can rapidly propagate through the substrate while the surrounding material simply shifts outwards. Therefore, unconstrained testing generally results in lower strength values than constrained testing.

It should be noted that the geometry of deposit samples can result in significant variability in macrohardness measurements. Specifically, macrohardness testing generally assumes the sample is flush with both the movable probe and the fixed plate. The validity of this assumption varies greatly depending on the size of the probe face, and the degree of roughness (OD) and curvature (ID) of the deposit surfaces. Further, the geometry of TTS collars and tube scale flakes makes constrained testing of these deposit types difficult. It is also noted that due to the

heterogeneous nature of TTS collars, there may be significant variability in macrohardness measurements from piece to piece, and numerous measurements may be required to obtain meaningful statistical information. This is another reason that microhardness measurements are generally preferred (many hardness measurements can be obtained for each TTS collar).

Other mechanical properties such as elastic modulus, fracture stress, thermal expansion, and swelling of steam generator tubing deposits have been measured using specimens and techniques adapted from conventional tests [26, 27]. These types of tests are not common, and require a suitable deposit sample that can be machined into the appropriate test specimen dimensions. Machined tubing scale has also been used to measure thermal expansion and conductivity of deposits removed from a steam generator [28].

3.3.2 Mössbauer Spectroscopy

As noted above, XRD is the most commonly used bulk analysis technique for distinguishing compound forms present in SG deposit samples. Although XRD is generally very effective for this purpose, it is very challenging to use XRD to distinguish two different compounds that have the same crystalline structure (e.g., magnetite and nickel ferrite) and similar lattice spacings. In most cases, confirmation that a spinel structure exists is sufficient to accurately identify the primary compounds present by XRD (see Section 3.2.4.2). However, in some cases, it may be useful to obtain additional confirmation of the presence of compounds with the same crystalline structure, by performing both XRD and Mössbauer spectroscopy. Mössbauer spectroscopy is an analytical technique capable of distinguishing two compounds with the same crystalline structure, but different electronic states. Relatively few elements of interest for SG deposit analysis are Mössbauer-active, with iron being by far the most commonly studied element. In the context of SG deposit characterizations, Mössbauer spectroscopy is most commonly used to distinguish magnetite (Fe_3O_4) from maghemite (γ-Fe_2O_3), an iron compound with similar crystalline structure as magnetite and the same chemical formula as hematite (α-Fe_2O_3).

In Mössbauer spectroscopy, a crystalline sample is irradiated with gamma rays from a radioisotope which decays into the isotope to be measured in the sample. In SG deposit characterizations, the most common source is the decay of ^{57}Co into ^{57}Fe. The energy of the source gamma rays is modulated slightly by moving the source relative to the sample at a range of speeds (taking advantage of the Doppler effect), and the fraction of the gamma rays which are absorbed by the sample at each speed (i.e., each slightly different source energy) is related to both the abundance and the oxidation state of the target isotope. Therefore, the spectrum collected (i.e., the fractional absorbance versus differential velocity) is characteristic of the specific compound (or compounds) present in the sample.

Mössbauer spectroscopy may also be performed on deposits collected on feedwater filters during startup and at various points during the operating cycle, and the observed oxidation state of these deposits may provide insight into the feedwater conditions.

3.3.3 Differential (Gas/Water) Pycnometry and Mercury Porosimetry

As noted previously, image analysis is the preferred method for measuring the porosity of SG deposits (see Section 3.2.3.2). However, pycnometry can also be used as a complementary technique if desired.

Pycnometry is used to accurately measure the volume of irregular solids through the displacement of either a gas or a liquid. Combined with a sample mass, this allows for the direct calculation of sample density. When a gas (typically helium) is used, voids/pores in the sample which are in communication with the surface of the sample are filled and the sample volume measured represents only the physical material and voids not connected to the sample surface (i.e., the sample "skeleton"). When water is used, surface tension prevents the filling of small pores (< 1 mm diameter) and the sample volume measured represents the bulk sample. Therefore, the porosity of a sample can be calculated as the difference in sample volumes measured by liquid and gas pycnometry divided by the sample volume measured by liquid pycnometry. Porosity measurements obtained by pycnometry are generally consistent (within 10-20%) with those obtained by image analysis. However, soft cleanings and other applications that lead to the structural modification of SG tube scale (particularly in the exterior pores) can result in inaccuracies in porosity measurements based on differential pycnometry when pore sizes increase to the point that surface tension is no longer sufficient to prevent water from partially filling the exterior pores (see additional discussion in Section 3.2.3.2).

Mercury porosimetry is a related technique in which liquid mercury is forced into the sample under increasing pressure (from vacuum to as high as 60,000 psi). As the pressure increases, the pore size the mercury is capable of entering decreases (smaller pore diameters correspond to a greater surface tension). Therefore, measurements of the mercury volume introduced versus the overpressure applied can be used to calculate the distribution of pore diameters. Additionally, the initial and final volumes of mercury can be used to calculate the bulk and skeletal volumes of the sample, respectively, allowing for calculation of the overall porosity (neglecting pores/voids which are not in communication with the sample surface). Finally, knowledge of the distribution of pore diameters and the total void volume (e.g., the bulk volume minus the skeletal volume) allows for calculation of the specific surface area. It is a noted that mercury porosimetry is considered a destructive examination technique in that performing this technique on a deposit sample renders the deposits unusable for subsequent analyses.

All of the data above can also be accurately and conveniently obtained through image analysis (see Section 3.2.3.2).

3.3.4 BET (Specific Surface Area) and Dye Adsorption

The adsorption of inert gases (typically nitrogen or krypton) on surfaces at very low temperatures can be related to the specific surface area of the substrate through the assumption of a Brunauer-Emmett-Teller (BET) isotherm. This technique is used to measure the specific surface area of SG deposits. Surface area can also be accurately and conveniently obtained using image analysis (see Section 3.2.3.2).

Dye adsorption techniques can also be used to measure the specific surface area of deposits. An isotherm for the adsorption of dye by deposits in a liquid solution can be determined by measuring the dye concentration before and after adsorption. However, as discussed in Section 3.3.3, liquids may not readily penetrate small deposit pores. Therefore, dye adsorption techniques may understate the specific surface area of SG deposits unless care is taken to ensure that all pores are filled (e.g., through the application of an overpressure to force liquid into the pores). This technique has been used during deposit characterization studies in the past, but is no longer routinely used since other techniques are convenient and effective for this purpose (e.g., image analysis).

3.3.5 Transmission Electron Microscopy (TEM)

As with scanning electron microscopy, transmission electron microscopy (TEM) is an imaging technique based on interaction of energetic electrons with the sample. In TEM, a contrast image is generated by collecting electrons from the original beam which have passed through an ultrathin specimen (on the order of 100 nm thick). TEM is capable of achieving higher magnification and resolution than SEM (with 2 Å resolution common in older conventional TEMs and atomic resolution achievable on more modern instruments). However, sample preparation is significantly more difficult and higher magnifications than those achievable by SEM are typically not necessary for deposit characterization. For these reasons, SEM is preferred for most SG deposit characterization studies.

Similar to SEM-EDS, analytical transmission electron microscopy (ATEM) is a technique that can be used to measure electron energies and compositional information at very specific locations and with much higher spatial resolution. Because ATEM is capable of much greater resolution than SEM-EDS, it is particularly useful for compositional studies of crack tips (as might be performed as part of the destructive examination of a pulled tube). While this sourcebook focuses on the ex-situ characterization of deposits removed for SGs, pulled tube examinations are discussed briefly in Section 3.4.2.

3.3.6 Auger Electron Spectroscopy and Secondary Ion Mass Spectrometry (SIMS)

As discussed in Section 3.2.3.3, when an atom is bombarded by electrons and a secondary electron is ejected from an inner orbital, a higher energy electron will relax into the lower energy electron hole and emit an X-ray in the process. If that X-ray excites and ejects another electron from the atom, this electron is referred to as an Auger electron. Auger electron spectroscopy is a technique which studies these electrons to determine sample composition. As with SEM-EDS, Auger electron spectroscopy provides information on the surface composition only[3]. (Because the mean free path of an electron (which is also relatively very low energy) through a material is much smaller than an X-ray photon, Auger electrons come from the top few angstroms of the sample.) If a compositional depth profile is desired, ion milling (to remove successive surface layers) is employed in addition to the spectroscopy. This is more common for Auger electron

[3] SEM-EDS penetrates on the order or 2 microns into the deposit surface, while Auger electron spectroscopy penetrates on the order of 1 to 3 nm. While the penetration depths are different orders of magnitude, they are both considered surfaces analyses in the context of analysis of deposit pieces since tube scale flakes are generally on the order of 100 microns thick or larger, and TTS collars are typically several mm thick. EPRI 1021113 provides a discussion of analytical techniques with a focus on surface penetration [30].

spectroscopy, than SEM-EDS. In case of SEM, this ion milling is typically done by a liquid Ga source. Such an instrument is called a focused ion beam scanning electron microscope (FIB-SEM), and offers excellent possibilities for in-situ cross-sectioning and imaging of small areas of SG deposits.

Secondary ion mass spectrometry (SIMS) is another technique for measuring surface composition and depth profiles. SIMS utilizes an ion beam (typically Ar or Cs) to sputter off thin layers of the specimen, which are then collected and analyzed in a mass spectrometer to determine the composition. (Mass spectrometry is discussed in more detail in Section 3.2.4.1, above).

3.3.7 X-ray Fluorescence (XRF) and X-ray Photoelectron Spectroscopy (XPS)

Energy dispersive X-ray fluorescence (EDXRF) and wavelength dispersive X-ray fluorescence (WDXRF) are similar to SEM-EDS and SEM-WDS in that the energy or wavelength, respectively, of X-rays emitted when higher energy electrons fall into lower orbitals is measured to determine composition. Unlike SEM compositional techniques, in XRF the excitation energy used to create the electron hole in the lower orbital is provided by an X-ray source rather than by electron bombardment. XRF provides bulk elemental composition, but is not as quantitative as ICP and does not provide the compound information given by XRD.

X-ray photoelectron spectroscopy (XPS, also known as electron spectroscopy for chemical analysis, or ESCA) is another technique which utilizes an X-ray source (typically Mg or Al Kα X-rays) to excite an atom for the purpose of measuring composition and oxidation state. Unlike XRF, XPS measures the energy of electrons which are emitted due to the X-ray excitation rather than the X-rays which are emitted. The electrons emitted during XPS, like Auger electrons, are relatively low energy. Because of this, only electrons from the top 1-10 nm of a sample escape and are detected. Therefore, XPS is a surface analysis technique and must be coupled with a milling technique if a depth profile is desired. The energy of the emitted electrons is sensitive to the chemical state of the surface compound allowing for XPS to be able to detect the chemical form of the surface layers. One use for XPS is to differentiate oxide form of the surface layers such as separating out NiO from $Ni(OH)_2$.

3.3.8 Raman Spectroscopy and Infrared (IR) Spectroscopy

Raman spectroscopy measures the inelastic scattering of a monochromatic light beam by a sample in order to study the vibrational modes of the compounds in the sample. As vibrational modes are characteristic of a compound, Raman spectroscopy can be used to identify the compounds in a sample.

Infrared (IR) spectroscopy measures the absorption of infrared light as a function of the light frequency. IR absorption frequencies also depend on the vibrational modes of the compounds in the sample, and thus can also be used in compound identification.

Fourier transform infrared (FTIR) spectroscopy is a type of IR spectroscopy in which the sample is exposed to a group of wavelengths of infrared light simultaneously (rather than scanning through the wavelengths sequentially using a moving prism, as is done in the now-obsolete standard IR spectroscopy) and measuring the overall absorption for the group. After exposing the sample to several different groupings of wavelengths, a Fourier transform (a mathematical

process for converting between time and frequency space) is used to recover the absorption as a function of wavelength (or wavenumber). In general, FTIR spectroscopy allows for better resolutions and/or faster scan times than standard IR spectroscopy.

3.3.9 Ion Exchange (IX) Chromatography for Leachable Ions

Determination of leachable ions (SO_4^{2-}, Cl^-, etc.) can provide information regarding the presence of potentially corrosive species. These species are generally present at very low concentration within SG deposits and may be of limited interest during SG deposit characterization studies. However, if these species are of particular interest (e.g., following a condenser leak or in support of a material degradation assessment), ion exchange (IX) chromatography can be used to analyze for these species. Ions are first leached from the deposits by placing a small quantity of deposits in a beaker with deionized water and then placing the beaker into an ultrasonic water bath for approximately one hour. IX chromatography is then used to determine the concentration of the leached ions. Deposits may also be leached in deionized water at approximately 100°C for a minimum of one hour. IX chromatography is performed by passing the sample over a resin that will retain the analytes (i.e., the leached ions) for different periods of time depending on their charge, allowing the concentrations of ions to be individually measured in the effluent from the resin bed.

3.3.10 Total Carbon Analysis

Total carbon analysis of deposit samples can be readily accomplished through combustion of the sample in oxygen and measurement of the CO_2 content by gas chromatography or thermal conductivity. Wet oxidation followed by infrared spectroscopy to measure the resultant CO_2 may also be used to measure the total carbon in a sample [31].

3.3.11 Total Sulfur Analysis

Several different techniques can be used to measure the total sulfur in a deposit sample, including sample combustion and measurement of the SO_2 produced, wet oxidation and measurement of the SO_4^{2-} produced, and sample digestion and measurement by ICP, as discussed in Section 3.2.4.1 [31].

3.3.12 Magnetic Susceptibility

As the magnetic properties of deposits depend on their crystalline state, whether or not they respond to magnetic fields can provide some limited information regarding their compound form. For example, magnetite and maghemite respond to magnetic fields (they are ferrimagnets), while hematite only responds weakly to magnetic fields (it is a canted antiferromagnet).

3.3.13 Radiography

Radiography is a technique which measures the attenuation of X-rays passed through deposits in order to determine the density of deposit material.

3.3.14 Neutron Activation Analysis

Neutron activation analysis is a process for determining the elemental composition of a sample. In neutron activation analysis, the sample is bombarded with neutrons, leading to neutron activation of elements within the sample. The characteristic gamma rays emitted upon decay of the activated elements are measured to determine composition.

3.4 Related Activities

The focus of this sourcebook is the ex-situ characterization or analysis of the chemical and physical properties of deposits removed from the secondary side of PWR SGs (e.g., during sludge lancing). However, there are number of other related activities that provide information about SG deposits and/or that produce data that can be used in combination with SG deposit characterization studies to gain insight into the condition of the SGs or optimize deposit management strategies. These activities are discussed in the sub-sections that follow.

3.4.1 NDE

In-situ non-destructive examination (NDE) techniques are routinely used by SG service vendors and can provide additional information regarding the nature, extent, loading and distribution of SG deposits which can inform decisions regarding deposit removal procedures. For example, low frequency eddy current testing (ECT) can be used to estimate the thickness and distribution of deposits present on the outside diameter of SG tubing and within TSP quatrefoils [38]. ECT techniques can also be used to assess the height of hard sludge collars present at the TTS. Further, copper present in SG deposits can interfere with ECT signals. Thus, it may be possible to make qualitative assessments regarding the composition of SG deposits based on ECT data.

Based on the above, utilities should consider NDE results, along with the results of deposit characterization studies, when assessing the overall condition of the SGs. Nonetheless, the practical application of in-situ NDE techniques is significantly different than the practical application of ex-situ SG deposit characterization techniques. Further, in-situ NDE techniques are discussed in detail in other industry references [32, 33, 34, 35]. Thus, NDE techniques are not discussed in detail in this sourcebook.

3.4.2 Pulled Tube Examinations

Deposit characterization studies are also closely related to destructive examination of pulled tubes. Analysis of deposits on pulled tube surfaces can provide particularly useful information about the chemistry conditions at the tube scale-to-tube interface and within tube cracks, and some of the techniques that may be utilized for this purpose are discussed herein (see Section 2.1.2.2). Further, other techniques discussed in the context of ex-situ characterization of SG deposits may also be used for destructive examination of pulled tubes (e.g., cross-section and examination techniques discussed in Sections 3.2.3 and 3.3.5). Nonetheless, pulled tube examinations are not discussed in detail in this sourcebook because separate guidelines already exist for the examination of pulled tubes [36].

3.4.3 Chemical Cleaning Qualification Testing

As noted in earlier sections, analyzing the chemical and physical properties of SG deposits as part of a SG deposit characterization study may assist in the development of an optimal SG chemical cleaning process. However, SG deposit samples may also be used in laboratory testing to evaluate the efficacy of this cleaning process and qualify the process for on-site use at the plant of interest. This is typically accomplished by exposing relevant deposit types (e.g., powdered sludge, tube scale, TTS collars, etc.) found in recent deposit samples to a laboratory simulation of the proposed cleaning process. Depending on the type of cleaning process, SG deposits may also be recharacterized (using the techniques discussed above) to assess the impact of the process on deposit properties (e.g., structural modification of SG tube scale observed in qualification testing may be used to project the expected heat transfer benefit of a soft cleaning process).

3.4.4 On-line Measurements

Some properties of steam generator deposits can be characterized on-line during operation. For example, an increase in tube fouling and/or a decrease in tube scale porosity may decrease secondary side steam pressure, which is a potential cause of lost generating capacity in PWRs. However, power uprates, primary temperature changes or errors, tube plugging, flow streaming and other factors can also affect secondary side steam pressure. In accordance with the industry-accepted methodology discussed in EPRI TR-110018, these factors must be considered when determining the extent to which steam generator pressure changes are attributable to secondary side deposits [37].

In addition, the distribution of deposits within broached hole tube support plate openings may be ascertained through measurements of wide range level. Steam generator wide range level is an indicator of the thermal-hydraulic resistance as fluid flows upward within the tube bundle, and wide range level has been correlated to tube support plate blockage using empirical models [38].

4
DATA INTERPRETATION AND OTHER CONSIDERATIONS

The practices discussed in Section 3.2 reflect those utilized during most routine deposit characterization studies. However, the exact work scope and the manner in which data is interpreted depend to some extent on the purpose and objectives of the study. These considerations are generally discussed throughout Section 3. However, the following additional comments are made:

- Deposit characterizations are generally performed for one or more of the following reasons:
  - Proactive assessment of the condition of the SGs (e.g., nature of deposits present, presence of foreign material, trends in deleterious species, potential risk of tubing degradation, etc.),
  - Diagnosis of specific material degradation issues (e.g., TTS denting),
  - Evaluation of thermal performance changes, and/or
  - In preparation for maintenance activities (e.g., SG chemical cleaning).
- When a deposit characterization is being performed primarily to assess TTS denting, attempts should be made identify and segregate any TTS collars found in the as-received deposit samples. Comprehensive analysis (e.g., cross-sectioning and compositional analysis) should be performed on as many TTS collars as possible, while considering that some of the mass of TTS collars may also be required for other activities (e.g., SG chemical cleaning qualification testing). Because the two postulated mechanisms for denting both involve the corrosive expansion of carbon or low alloy steel (i.e., metallic debris that has become embedded within the collars, or the tubesheet itself), attempts should be made to determine if such corrosion-susceptible metallic inclusions are present within the collars and/or if the shape of the collar provides an insight into the possible corrosive expansion of the tubesheet. Any observations that relate to possible mechanisms for TTS denting should be provided in the deposit characterization report. Deposit samples should also continue to be collected, characterized and retained until the plant resolves the denting issue.
- SG tube scale is the primary deposit type of interest when deposit characterization studies are performed in support of SG thermal performance evaluations. As such, more extensive tube scale structural evaluations may be appropriate when deposit characterizations are performed for this purpose, and close attention should be paid to tube scale sub-layers (regions of higher or lower porosity present throughout the thickness of the scale), which are important for overall heat transfer. Similar considerations apply when deposit characterizations are performed in support of soft cleaning applications designed to improve heat transfer. Tube scale structure is generally evaluated in the as-received condition and then again after

chemical cleaning qualification testing to assess the impact of the proposed soft cleaning on the deposit characteristics. The observed change in tube scale structure can then be used to predict the heat transfer benefit (e.g., steam pressure increase) expected as a result of the soft cleaning operation.

- When performed in support of "hard" chemical cleaning preparations, tube scale and TTS collars are the primary deposit types of interest during deposit characterization studies. Tube scale generally accounts for a majority of the deposit mass in the SGs. While TTS collars may account for a relatively small fraction of the overall mass, removal of TTS collars during SG chemical cleaning operations and other maintenance activities is important due to the role of TTS collars in tubesheet degradation mechanisms such as denting. Comprehensive analysis (e.g., cross-sectioning and compositional analysis) should be performed on as many tube scale flakes and TTS collars as possible, while considering that some of the mass of these deposits may also be required for other activities (e.g., SG chemical cleaning qualification testing).
- In addition to deposit structure and chemistry, overall deposit loading is an important input to the development of an effective SG chemical cleaning process. The thickness and porosity of SG tube scale (as measured during a deposit characterization study) can be used to estimate the overall deposit loading present in the SGs. However, tube scale flakes found in as-received deposit samples may not necessarily be representative of scale found on all heat transfer surfaces. Thus, it is important to generate deposit loading estimates using several independent techniques (e.g., based on feedwater impurity transport, scale profiling based on low-frequency ECT, etc.), and to compare these results. The possibility of non-uniform distribution of tube scale throughout the tube bundle must also be considered in thermal performance evaluations performed in conjunction with deposit characterizations.
- Recommendations for species to be measured during compositional analyses are based on the species most commonly found in SG deposit samples. Depending on plant operating experience, it may be necessary to analyze for additional species and/or to provide additional data interpretation. For example, IX chromatography may be particularly useful following a condenser leak, and closer examination and analysis of trends in copper, lead or other deposit species may be required following significant plant events (e.g., replacement of copper bearing components in BOP systems, gross contaminant ingress such as a lead blanket being left behind in a SG, etc.).
- Observations regarding small loose parts and/or foreign objects should be noted in the deposit characterization report, particularly if the plant has experienced degradation associated with loose parts wear.

The comments above should be considered when determining an appropriate scope for a deposit characterization study, and when interpreting the data obtained, to ensure that utility objectives are met.

5
SURVEY OF CURRENT UTILITY PRACTICES

Section 5.1 discusses utility responses to a survey of plant practices regarding deposit sampling and characterization. Section 5.2 reviews several deposit characterization studies published in the literature since the predecessor to this sourcebook (TR-106048) was issued.

5.1 Utility Survey

In support of preparation of this sourcebook, a survey regarding deposit sampling and characterization practices was distributed to a number of foreign and domestic utilities. A blank copy of the survey is included as Appendix A. It is noted that this survey also contains questions regarding chemistry control and sludge management practices. However, responses to these questions are discussed in detail in Reference [6] and are therefore not repeated herein.

Survey responses were received from 81 operating units. A breakdown of respondents by country is provided in Table 5-1. Survey responses are summarized in Table 5-2 through Table 5-6. Because the current survey distributed in support of this sourcebook is similar to that previously distributed in support of TR-106048, responses to the current survey are compared to the prior survey in order to assess any changes in practices. (A total of 28 units representing both foreign and domestic utilities responded to the prior survey.) The following observations are made based on a review of utility survey responses:

- The majority of responding utilities (67%) characterize SG deposits collected during each sludge lancing campaign (up from 43% in the previous survey), and an additional 15% of responding utilities periodically characterize SG deposits. Very few utilities indicate that they have no plans to characterize SG deposits.
- As was the case in the previous survey, the vast majority (89%) of responding utilities reported that SG deposit samples are obtained from sludge lancing filters. Several utilities reported using more than one sampling method.
- Consistent with the previous survey, responding utilities reported that sample sizes were typically in the range of 1 g to 1 kg.
- Approximately 40% of the responding utilities reported archiving samples (or having samples archived by a vendor). Significant variability was observed in the reported archiving period.
- As was the case in the previous survey, nearly all responding utilities reported analyzing samples for elemental composition. The percentage of responding utilities which reported analyzing samples for compounds present nearly doubled compared to the previous survey (68% vs. 36%). Substantial increases in the percentage of utilities performing other types of chemical analyses were also observed.

- Significant increases in the percentage of responding utilities analyzing deposit physical properties were also observed relative to the previous survey. The most commonly analyzed physical properties of SG deposits were density, porosity and tube scale thickness.

Overall, survey responses indicate that there has been a significant increase in the utility focus on deposit characterization since the previous industry survey in 1996. The increase in deposit collection/characterization frequency and types of analyses being performed to analyze deposit chemical and physical properties is consistent with the perspective that SG deposit properties play an important role in SG integrity and performance, and that routine characterization of deposit properties is therefore critical to overall SG management. Greater standardization of practices for archiving SG deposit samples was identified as one possible area for improvement based on this survey, and guidance on sample archiving has been added in this sourcebook (see Section 2.2.4).

Table 5-1
Breakdown of Utility Respondents by Country

Country	Number of Units	Percentage of Respondents
USA	49	60%
Canada	11	14%
Belgium	7	9%
South Korea	6	7%
Spain	5	6%
Sweden	3	4%

Table 5-2
Deposit Characterization Practices

Deposit Characterization Practices		Current Survey	TR-106048 Survey
Frequency of Deposit Characterization	Always	67%	43%
	Occasionally	15%	14%[a]
	Never - Plan to in Future	11%	-
	Never - Do Not Plan to in Future	7%[b]	-
Have Performed Deposit Characterization at least Once		81%	>75%
Deposit Characterization Part of Sludge Lancing Contract		36%	25%

a) Only includes deposit characterization by organizations other than sludge lancing vendor.
b) All six units indicated that they would perform deposit characterization if required as part of a tube removal analysis.

Table 5-3
Sampling Methods

Sampling Location / Method (Used or Planned)		Current Survey	TR-106048 Survey
Only One Sampling Location / Method Indicated		75%	-
Two or More Sampling Locations / Methods Indicated		22%[a]	-
No Sampling Locations / Methods Indicated		2%	-
Sampling Location / Method[b]	Tubesheet Sludge Lancing Filters	89% (67%)[b]	96%
	Pulled Tubes[c]	15% (7%)[b]	18%
	Tube Scale	10% (0%)[b]	14%
	Tubesheet Region (Manual)	7% (1%)[b]	18%
	Separator/Dryer Region	5% (0%)[b]	-
	Chemical Cleaning or Pressure Pulse Filters	4% (0%)[b]	15%
	Upper Bundle	4% (0%)[b]	-
	In Bundle Tubesheet	1% (0%)[b]	-
	Annulus Sludge	1% (0%)[b]	-
	Flow Distribution Baffle	0% (0%)[b]	4%
	Broached Hole	0% (0%)[b]	-
	Performed by Vendor, Unsure of Method	6% (1%)[b]	

a) All 18 of these units indicated tube sheet sludge lancing filters were one of their sampling locations.
b) Parenthetical value is percentage of units which reported location/method as the only location/method utilized.
c) Although the survey specified “other (e.g., pulled tubes),” all of the units who selected this option on the current survey clarified that pulled tubes were specifically being referenced.

Table 5-4
Sample Size and Storage/Handling of Deposit Samples

Storage/Handling of Deposit Samples		Current Survey	TR-106048 Survey
Typical Sample Size		47%	-
Results - Typical Sample Size	Minimum	1.5 grams	< 1 gram
	Average	360 grams	-
	Maximum	1000 grams	1000 grams
Samples Stored in Sealed Containers		68%	-
Only Wet Samples Stored		32%	-
Only Dry Samples Stored		25%	-
Both Wet and Dry Samples Stored		15%	-
Samples Stored in Inerted Containers		1%	-
Entire Filters Sometimes Sent for Analysis		2%	-
Typical Radiation and/or Activity Level		32% (11%)[a]	-
Unsure of Typical Radiation or Activity Level		31%	-
No Response		37%	-
Typical Radiation Level		27%	-
Results - Typical Radiation Level	Zero or Approximately Zero	19%	-
	0.02 mR/hr	4%	-
	Less than 1 mR/hr	4%	-
	Less than 2 mR/hr	1%	-
Typical Activity Level		16%	-
Results - Typical Activity Level	Zero or Approximately Zero	11%	-
	1×10^{-6} µCi	2%	-
	2×10^{-3} µCi	1%	-
	3×10^{-3} µCi	1%	-
Samples Archived by Utility and/or Vendor		40% (11%)[b,c]	-
Samples Disposed of Following Analysis		35%[b]	-
No Response		28%	-
Samples Archived by Utility		25%	-
Utility Archiving Period	≤ 5 Years	5%	-
	> 5 and ≤ 10 Years	6%	-
	> 10 and ≤ 25 Years	2%[b]	-
	Indefinitely	6%	-
	Not Reported	5%	-
Samples Archived by Vendor		26%	-
Vendor Archiving Period	≤ 5 Years	11%	-
	Indefinitely	9%	-
	Not Reported	6%	-

a) Parenthetical value is percentage of units which reported both typical radiation level and typical activity level.

b) Two units indicated that samples were both disposed of after analysis and archived for >10 and ≤25 years.

c) Parenthetical value is percentage of units which reported both utility and vendor archive sample.

Table 5-5
Chemical Properties of Deposits

Chemical Properties of Deposits		Current Survey	TR-106048 Survey
Chemical Analysis Methods	Elemental Composition (e.g. Iron, Copper, Zinc)	95%[a]	89%
	Trace Elements (e.g., Chloride, Lead, Sulfur)	73%	61%
	Compounds (e.g., Magnetite, Hematite, Copper oxides)	68%	36%
	Carbon Content	59%	21%
	Leachable Chlorides, Sulfates	46%	25%
	Reduced Sulfur Species	22%	4%
	Formates, Acetates	0%	36%
	Did Not Respond to Chemical Analysis Methods Questions	5%[a]	-
Results - Elements / Compounds Detected	Magnetite, Iron/Zinc spinels, and/or Iron/Nickel Spinels	53%[b]	-
	Lead	48%	39%
	Titanium	31%	-
	Copper Oxide > Copper Material	27%	-
	Sulfur Species	25%	-
	Calcium and/or Phosphate Compounds	23%	18%
	Manganese > 1 wt%	21%	-
	Hematite > 5 wt%	4%	4%
	Zinc > 10 wt%	4%	-
	Did Not Respond to Chemical Analysis Results Questions	37%	-

a) The four units which did not indicate that they analyzed the elemental composition did not provide any answers in this section of the survey.

b) Magnetite (and substituted spinels) is expected to be the main deposit constituent in most SGs. The percentage reported here is thought to be low due to a lack of responses to this section of the survey.

Table 5-6
Physical Properties of Deposits

Physical Properties of Deposits		Current Survey	TR-106048 Survey
Physical Analysis Methods	Density	51%	21%
	Porosity / Skeletal Density	44%	11%
	Thickness of Tube Scale Flakes	37%	-
	Particle Size Distribution	27%	-
	Pore Size Distribution	20%	4%
	Specific Surface Area	16%	7%
	Magnetic Properties	6%	4%
	Hardness	0%	11%
	Thermal Conductivity	0%	-
	Did Not Respond to Physical Analysis Methods Questions	42%	-
Results - Sludge Properties	Mostly Powdery Sludge	59%	-
	Very Hard Sludge	37%	-
	Tube Scale with Layers	11%	-
	Tube Scale with Significantly Different Properties Compared to Tube Sheet Sludge	4%	-
	Significant Variation Outage to Outage	0%	-
	Did Not Respond to Physical Analysis Results Questions	19%	-

5.2 Literature Review

Table 5-7 summarizes references that relate to SG deposit characterization which have been published since the predecessor of this sourcebook (TR-106048) was issued. A summary of older references is available in TR-106048.

Table 5-7
Deposit Characterization References

Date	Reference	Topic
5/11/1994	A. Barkatt, E. Labuda, G. Cherepakhov, R. Burns, *Characterization of Sludge from Indian Point 2* , in *Proceedings: Steam Generator Sludge Management Workshop.* EPRI, Palo Alto, CA: 1994. TR-104212.	Deposit Characterization, Single Plant
5/11/1994	J. Semmler, R. A. Speranzini, *Characterization of Bruce A-U2 and Pickering B-U5 Steam Generator Secondary Side Deposits* , in *Proceedings: Steam Generator Sludge Management Workshop.* EPRI, Palo Alto, CA: 1994. TR-104212.	Deposit Characterization, Multiple Plants
8/20/1996	J. Semmler, D. A. Guzonas, *Characterization and Dissolution Studies of Bruce Unit 3 Secondary Side Loose Deposits and Flakes* , in *Proceedings: Steam Generator Sludge Management Workshop.* EPRI, Palo Alto, CA: 1996. TR-108047.	Deposit Characterization, Single Plant
8/20/1996	A. Barkatt, E. Labuda, M. Gmurczyk, G. Cherepakhov, R. Burns, *Characterization of Nature and Mobility of Corrosive Species in Steam Generator Sludge* , in *Proceedings: Steam Generator Sludge Management Workshop.* EPRI, Palo Alto, CA: 1996. TR-108047.	Deposit Characterization, Single Plant
1/1/1997	A. M. Lancha, D. Gomez-Briceno, M. Garcia-Mazario, C. Maffiotte, *Characterization of Ringhals 3 TSP Crevice and Tube Deposits,* in *Proceedings of the Eighth International Symposium on Environmental Degradation of Materials in Nuclear Power Systems - Water Reactors - Volume 1,* Amelia Island, FL, 1997.	Deposit Characterization, Single Plant
7/1/1997	R. D. Varrin, *Cost-Benefit Evaluations of Secondary Side Deposit Removal and Control Strategies,* in *Proceedings: Steam Generator Sludge Management Workshop, Myrtle Beach, South Carolina, August 19-21, 1996,* EPRI, Palo Alto, CA, 1997. TR-108047.	SG Planning
7/15/1997	*Oconee Unit 2 Steam Generator Tube Examination,* EPRI, Palo Alto, CA, 1997. TR-106863.	Deposit Characterization, Single Plant
9/1/1997	M. A. Kreider, G. A. White, R. D. Varrin, P. J. Ouzts, *Heat Transfer Characteristics of Porous Sludge Deposits and Their Impact on the Performance of Commercial Steam Generators,* DEI, VA, 1997. DEI-518.	Deposit Characterization, Multiple Plants
3/14/1998	F. Cattant, *Chemical Analysis of OD Deposits Removed from SG Tubes,* in *Proceedings: 1993 EPRI Workshop on Secondary-Side IGA/SCC,* EPRI, Palo Alto, CA, 1998. TR-107883.	Deposit Characterization, Multiple Plants
9/14/1998	B. Sala, A. Gelpi, S. Chevalier, M. Dupin, *Complementary Investigations Concerning the Analyses of the Deposits and Underlying Surfaces Observed on French PWR Steam Generator Pulled Out Tubes,* in *Contribution of Materials Investigation to the Resolution of Problems Encountered in Pressurized Water Reactors,* Proceedings of the International Symposium, Fontevraud IV, 1998.	Deposit Characterization, Multiple Plants
9/14/1998	A. M. Lancha, D. Gomez-Briceno, M. Garcia-Mazario, C. Maffiotte, A. McIlree, *Characterization of Crevice Deposits in Ringhals 3 Steam Generator Tubes,* in *Contribution of Materials Investigation to the Resolution of Problems Encountered in Pressurized Water Reactors,* Proceedings of the International Symposium, Fontevraud IV, 1998.	Deposit Characterization, Single Plant
11/1/1998	J. A. Gorman, *Incorporation of TiO Inhibitor into Callaway Steam Generator Deposits,* Presented at the *EPRI PWR Plant Chemistry Workshop,* Huntington Beach, CA, 1998.	Deposit Characterization, Single Plant
1/1/1999	S. Chevalier, M. Organista, B. Sala, A. Gelpi, R. Erre, *Study of Deposits and Corrosion Products in Secondary Side of Steam Generators by Fourier Transform Infra Red Spectroscopy: Laboratory Study,* in *Proceedings of the Ninth International Symposium on Environmental Degradation of Materials in Nuclear Power Systems - Water Reactors,* Newport Beach, CA, 1999.	Analytical Technique - FTIR

Table 5-7 (continued)
Deposit Characterization References

Date	Reference	Topic
3/1/1999	S. Pagan, *Investigation of Bruce-A Steam Crevice Environment: Results and Comparison of Hideout Return, Deposit and Crack Analysis Evaluations,* in *Proceedings: 1996 EPRI Surface Chemistry Workshop,* EPRI, Palo Alto, CA, 1999. TR-112481.	Deposit Characterization, Single Plant
3/1/1999	R. Baker, S. Daniel, *A Comparison of the Chemistry Analysis of Steam Generator Tube Crevice Deposits with Operational Chemistry at the South Texas Project,* in *Proceedings: 1996 EPRI Surface Chemistry Workshop,* EPRI, Palo Alto, CA, 1999. TR-112481.	Deposit Characterization, Single Plant
3/1/1999	*Characterization of Ringhals 3 Tube Support Plate Crevice and Tube Deposits,* EPRI, Palo Alto, CA, Vattenhall Ringhals: 1999. TR-112110.	Deposit Characterization, Single Plant
9/30/1999	E. Frese, J. Eastwood, B. Cyrus, B. Fender, *Virginia Power Steam Generator Deposit Characterization and Maintenance Planning* , in *Proceedings: Steam Generator Sludge Management Workshop.* EPRI, Palo Alto, CA: 2000. TR-114854.	Deposit Characterization, Multiple Plants
4/1/2000	M. A. Kreider, G. A. White, R. D. Varrin, *Effects of Secondary Deposits on SG Thermal Performance: 1999 Update,* in *Proceedings: Steam Generator Sludge Management Workshop, Scottsdale, Arizona, September 30-October 1, 1999,* EPRI, Palo Alto, CA, 2000. TR-114854.	SG Planning
5/1/2001	J. Barkich, *Secondary Chemistry Assessments in Support of SG Deposit Management,* in *Proceedings: 2001 PWR/BWR Plant Chemistry Meeting,* EPRI, Palo Alto, CA, 2001. 1001489.	Deposit Characterization Planning
4/22/2002	J. Stevens, B. Fellers, S. Orbon, *Steam Generator Deposit Control Program Assessment at Comanche Peak,* in *Chimie 2002 Proceedings: International Conference Water Chemistry in Nuclear Reactors Systems: Operation Optimization and New Developments Volume 3,* Avignon, France, 2002.	Deposit Characterization, Single Plant
5/5/2002	M. Chocron, A. M. La Gamma, R. Servant, M. Villegas, A. N. Fernandez, L. Ovando, *Steam Generators: Some Water Chemistry and Deposits Characterization Data,* in *Proceedings of the 4th CNS International Steam Generator Conference,* Toronto, Canada, 2002.	Deposit Characterization, Multiple Plants
9/1/2002	J. Bland, *A Mössbauer Spectroscopy and Magnetometry Study of Magnetic Multilayers and Oxides,* University of Liverpool, 2002.	Analytical Technique - Mössbauer Spectroscopy
1/19/2003	F. Garofalo, *Steam Generator Secondary Side Deposit Management Two Schools of Thought,* presented at the *Westinghouse Steam Generator Workshop,* Scottsdale, Arizona, 2003.	Deposit Characterization Planning
1/19/2003	J Barkich, *Elements of a Maintenance Approach to Steam Generator Deposit Management,* presented at the *Westinghouse Steam Generator Workshop,* Scottsdale, Arizona, 2003.	Deposit Characterization Planning
2/11/2003	B. Fellers, J. Stevens, R. Theimer, S. Nasrazadani, H. Namduri, *Secondary System Oxide Characterization Study at Comanche Peak* , in *Proceedings: 2003 Steam Generator Secondary Side Management Conference.* EPRI, Palo Alto, CA: 2003. 1008468.	Deposit Characterization, Multiple Plants
2/11/2003	B. Cyrus, R. Maggi, *Steam Generator Deposit Trends and Characterizations for Operating Nuclear Power Stations* , in *Proceedings: 2003 Steam Generator Secondary Side Management Conference.* EPRI, Palo Alto, CA: 2003. 1008468.	Deposit Characterization, Multiple Plants

Table 5-7 (continued)
Deposit Characterization References

Date	Reference	Topic
2/11/2003	H. Venz, *Investigation of SG-Sludge of the Beznau NPP* , in *Proceedings: 2003 Steam Generator Secondary Side Management Conference.* EPRI, Palo Alto, CA: 2003. 1008468.	Deposit Characterization, Multiple Plants
6/1/2003	R. D. Varrin, C. R. Marks, A. T. Pellman, O. Flores, R. Stanley, G. Gary, *Recent Experience with Secondary Side Deposit Characterization,* in *Proceedings: 2003 Steam Generator Secondary Side Management Conference,* EPRI, Palo Alto, CA, 2003. 1008468.	SG Planning, Analytical Techniques
6/1/2004	C. Marks, *Some Effects of Steam Generator Deposits on Crevice Chemistry,* in *Proceedings of the USNRC/EPRI/ANL Heated Crevice Seminar,* EPRI, Palo Alto, CA, Office of Nuclear Regulatory Reasearch, Washington, D.C., and Argonne National Laboratory, Argonne, IL, 2004. 1009355.	Typical Deposit Characteristics
10/11/2004	B. Zhu, J. Chen, P. O. Andersson, *Post Investigations of Ringhals Steam Generator Tube Crevice Deposits,* in *Proceedings of the International Conference on Water Chemistry of Nuclear Reactor Systems: San Francisco, October 2004,* EPRI, Palo Alto, CA, 2005. 1011579.	Deposit Characterization, Single Plant
1/1/2005	S. Nasrazadani, H. Namduri, J. Stevens, R. Theimer, *Quantitative Morphological Characterization of Deposits Formed in the Secondary System of the Comanche Peak Steam Electric Station Using Scanning Electron Microscopy (SEM),* in *12th International Conference on Environmental Degradation of Materials in Nuclear Power Systems - Water Reactors, Volume 3: Papers 81-113,* Salt Lake City, Nevada, 2005.	Deposit Characterization, Single Plant
3/1/2006	N. van Eeden N, K. J. Galt, *Corrosion Product Sampling at Koeberg Nuclear Power Station,* PowerPlant Chemistry 2006, 8(3).	Deposit Sampling
11/26/2006	P. Luna, G. Diaz, H. Sveruga, R. Sainz, *Maintenance and Life Assessment of Steam Generators at Embalse Nuclear Station,* from *5th CNS International Steam Generator Conference,* Toronto, Ontario, Canada, 2006.	SG Planning
11/26/2006	R. Staehle, *Serious Concerns and Actions for Mitigating Future Degradation in Modern Steam Generators,* from *5th CNS International Steam Generator Conference,* Toronto, Ontario, Canada, 2006.	SG Planning
4/1/2007	S. Odar, V. Schneider, T. Schwarz, R. Bouecke, *Cleanliness Criteria to Improve Steam Generator Performance,* presented at the *International Conference on Water Chemistry of Nuclear Reactor Systems,* Jeju Island, Korea, 2006.	SG Planning
8/19/2007	P. J. King, J. Yu, S. Ramamurthy, W. Chang, K. Sedman, A. Lloyd, *Examination of Oxides and Deposits on Tubes Removed from Bruce Units,* presented at the *13th International Conference on Environmental Degradation of Materials in Nuclear Power Systems,* Whistler, B.C., Canada, 2007.	Deposit Characterization, Single Plant
6/8/2008	M. G. Pop, P. Shoemaker, K. Colgan, J. Griffith, *Steam Generator Asset Management Model Application,* in *Proceedings of the 2008 International Congress on Advances in Nuclear Power Plants: ICAPP '08,* held in Anaheim, CA, 2008.	SG Planning
9/15/2008	A. M. Olmedo, R. Bordoni, M. Miyagusuku, M. Chocron, N. Fernandez, D. Quinteros, L. Ovando, R. Sainz, *Oxide Measurements and Analyses of Deposits and Oxide Layers from the Secondary and Primary Sides of a SG Tube Removed from Embalse NPP,* presented at *NPC '08 Berlin, International Conference on Water Chemistry of Nuclear Reactor Systems,* held in Berlin, Germany, 2008.	Deposit Characterization, Single Plant
10/1/2008	M. A. Kreider, C. R. Marks, R. D. Varrin, *Secondary Water Chemistry, Iron Transport, and Steam Generator Fouling in US PWRs,* DEI, VA, 2008. DEI-980.	Deposit Characterization, Multiple Plants

Table 5-7 (continued)
Deposit Characterization References

Date	Reference	Topic
12/1/2008	*Steam Generator Management Program: Steam Generator Deposit Characterization for Steam Generator Tube Degradation Prediction and Management. EPRI, Palo Alto, CA, 2008. 1018249.*	Deposit Characterization, Multiple Plants
11/8/2009	M. A. Kreider, V. D. Moroney, G. A. White, R. D. Varrin, *Industry SG Heat-Transfer Fouling Trends and Probabilistic Fouling Predictions,* from *6th CNS International Steam Generator Conference Proceedings,* held in Toronto, Ontario, Canada, 2009.	SG Planning
11/8/2009	R. Bordoni, M. Chocron, M. Miyagusuku, A. M. Olmedo, A. Burkart, N. Fernandez, D. Quinteros, R. Sainz, *Characterization of Oxides and Corrosion on a Steam Generator Tube Removed from Embalse Steam Generator No. 3 after 7287 Effective Full Power Days,* from *6th CNS International Steam Generator Conference Proceedings,* held in Toronto, Ontario, Canada, 2009.	Deposit Characterization, Single Plant
1/1/2010	V. P. Woodward, R. C. Williams, Z. Amjad, *Chapter 21: Analytical Techniques for Identifying Mineral Scales and Deposits,* in Z. Amjad, *The Science and Technology of Industrial Water Treatment* , CRC Press, Boca Raton, FL, 2010.	Analytical Techniques
3/3/2010	I. Mailand, P. Franz, H. Venz, *Corrosion Product Measurement Program in the Secondary Circuit of Beznau NPP* , in *Proceedings: Steam Generator Management Program 2010 Steam Generator Secondary Side Management Conference.* EPRI, Palo Alto, CA: 2010. 1020915.	Deposit Characterization, Multiple Plants
4/1/2010	M. Vepsäläinen, *Deposit Formation in PWR Steam Generators,* VTT, Finland, 2010. VTT-R-00135-10.	SG Planning
10/3/2010	J. Semmler, D. Doyon, A. J. Lockley, *Analysis of Steam Generator Tube Sections Removed from Gentilly-2 Nuclear Generating Station,* from *NPC 2010 - Nuclear Plant Chemistry Conference 2010 Proceedings & 8th International Radiolysis Workshop Proceedings,* held in Quebec City, Canada, 2010.	Deposit Characterization, Single Plant
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2/1/2011	L.Weichel, T. Do, S. Stegall, A. Martin, *Engineering Optimized Steam Generator Maintenance Services* , presented at the *Westinghouse Steam Generator Workshop* , Scottsdale, Arizona, 2011.	SG Planning
3/13/2011	S.R. Zaidi, H. Sitepu, *Characterization of Corrosion Products in Oil and Gas Facilities using X-Ray Powder Diffraction Method,* presented at *NACE Corrosion 2011 Conference and Expo Proceedings,* held in Houston, TX, 2011.	Analytical Technique - XRD
8/7/2011	C. W. Turner, *Implications of Steam Generator Fouling on the Degradation of Thermal and Material Performance,* from *Proceedings of the 15th International Conference on Environmental Degradation of Materials in Nuclear Power Systems Water Reactors,* held in Colorado Springs, CO, 2011.	SG Planning
1/29/2013	L.Weichel, E. Morgan, *SG105 Secondary Side Cleanliness and Inspection Considerations* , presented at the *Westinghouse Steam Generator Workshop* , Scottsdale, Arizona, 2013.	SG Planning

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A
UTILITY QUESTIONNAIRE

Steam Generator Deposit Characterization Sourcebook Utility Questionnaire

Prepared by Dominion Engineering, Inc.

12100 Sunrise Valley Drive, Reston, VA 20191

Voice: 1.703.657.7300

Fax: 1.703.657.7301

e-mail: cmarks@domeng.com

Please contact Chuck Marks at Dominion Engineering, Inc. with questions or comments.

EPRI Project Manager
Heather Feldman, 1.704.595.2735, hfeldman@epri.com

Please return the completed form to EPRI (jma@epri.com) by September 1, 2011.

Please fill out a questionnaire for each unit unless practices at all units are essentially the same. Parts of this form have been completed for your convenience; please confirm these answers.

This information is being requested to support an EPRI Steam Generator Management Program project (TS TAC Project 1.2.10 "Deposits/Corrosion: Deposit Removal and Characterization and Sourcebook"). Information provided by utilities will be used in the EPRI Technical Reports associated with this project including an update to EPRI Report TR-106048 "Characterization of PWR Steam Generator Deposits"— the information will not be reproduced in the EPRI documents.

GENERAL

Your Name: _____ Plant: _____
Title: _____ Phone Number: _____
Utility: _____ FAX Number: _____
Email: _____

CHEMISTRY PROGRAM

Feedwater Chemistry Targets:
pH (typically) _____ since _____
Amine (ppb) _____ since _____
Hydrazine (ppb) _____ since _____

Plant Data:
_____ Number of Months in Cycle
_____ MWe
_____ Replaced/Will Replaced SGs in _____

Future Chemistry Plans:
___ Will be changing to _____ in _____

Purification Method:
___ Condensate Polishing
___ Full Flow
___ Partial Flow
___ Only during Startup/Transients
___ Blowdown Demineralization
___ % of Steam/FW Flow
___ Overboard Blowdown

UPDATE ON STEAM GENERATOR SLUDGE MANAGEMENT PRACTICES

Sludge Lancing ___ YES ___ NO

Frequency
_____ Each Refueling Outage
_____ Since Startup
_____ Since _____
_____ Alternate SGs each Refueling Outage
_____ Every _____ Refueling Outages for Each SG

Sludge Lance System (Vendors Used) _____

Typical Pounds Removed per SG _____ lbs/SG

Chemical Cleaning (CC) ___ YES ___ NO
Performed in _____ by _____
Planning to CC in _____
Type/Vendor _____

Pressure Pulsing/Water Slap ___ YES ___ NO
Performed in _____
Pounds Sludge Removed per SG _____ lbs/SG

Other Sludge Removal Processes
___ Top Bundle Washes
___ Other _____

SLUDGE CHARACTERIZATION PRACTICES

___ Have always performed or contracted sludge characterizations (each sludge lancing campaign)
___ Occasionally perform or contract for analyses
Vendor(s) _____
___ Included as part of sludge lancing by vendor
___ Do not perform or contract for sludge characterization
Plan to in future ___ YES ___ NO
___ Other _____

SAMPLING (check one or more)

___ Manual sampling from tube sheet region
___ Samples from filters/screens used by sludge lance vendor
___ Other (e.g., pulled tubes) _____
___ Samples from CC or pressure pulse filters
___ Upper bundle sampling
___ Samples from separator/dryer region
___ Tube scale sampling
___ In bundle tube sheet sampling
___ Annulus sludge sampling
___ Broached hole samples
___ Flow distribution plate samples
___ Performed by vendor, not sure of sampling method used

STORAGE AND HANDLING (check all that apply)

___ Typical sample size _____ grams
___ Sealed containers
___ Inerted containers (e.g., nitrogen cover)
___ Wet samples
___ Dried samples
___ Entire filters sometimes sent for analyses
___ Samples archived for _____ years by utility
___ Samples archived for _____ years by vendor
___ Samples disposed after analyses

Typical container contact radiation or activity levels _____ mR/hour _____ µCi ___ Not Sure

MEASURED CHEMICAL PROPERTIES (check all that apply)

___ Elemental analyses (e.g., iron, copper, zinc)
___ Trace elemental analyses (e.g., chloride, lead, sulfur, arsenic)
___ Compounds (e.g., magnetite, hematite, copper, copper oxides)
___ Leachable chlorides, sulfates
___ Carbon content
___ Formates, acetates
___ Reduced sulfur species
___ Other chemical properties of interest _____

IN THE PAST (CURRENT SGS), WE HAVE FOUND:

___ Calcium/phosphate compounds
___ Iron/zinc or iron/nickel spinels (e.g., magnetite)
___ Hematite >5 wt%
___ Copper oxides > copper material
___ Sulfur species
___ Lead
___ Manganese >1 wt%
___ Zinc >10 wt%
___ Titanium

MEASURED PHYSICAL PROPERTIES (check all that apply)

___ Density
___ Specific surface area (BET)
___ Porosity and/or skeletal density
___ Pore size distribution
___ Magnetic properties
___ Hardness
___ Flake thickness
___ Particle size distribution
___ Thermal conductivity

IN THE PAST (CURRENT SGS), WE HAVE FOUND:

___ Very hard sludge
___ Mostly powdery sludge
___ Tube scale with layers
___ Tube scale with significantly different properties compared to tube sheet sludge
___ Significant variation outage to outage

FUTURE PLANS

___ Plan to continue or start sludge characterizations
___ No plans to perform sludge characterizations

B
STEAM GENERATOR DEPOSIT TRANSPORT AND FORMATION

Although significant progress has been made in optimizing plant design and secondary water chemistry to minimize corrosion product transport (e.g., through removal of copper components and increased feedwater pH), it is inevitable that some corrosion products will form and be transported to the SGs. The purpose of this chapter is to briefly review the factors affecting the level of corrosion product transport and the deposits which form in the SGs. Additional information on this topic can be found in References [1] and [37].

B.1 Transport of Deposit Precursors

Deposit precursors are transported to the SGs from throughout the secondary system, and may be either particulate species, soluble ionic species, or soluble non-ionic species (including gases). Typical precursor materials include the following [1, 37]:

- Particulate, ionic, and soluble species liberated from corrosion films on piping, and heat exchanger and condenser surfaces. This is the greatest source of deposit precursors, and has been estimated to account for approximately 90% of the corrosion products transported to the SGs [40].
- Gaseous, ionic, particulate, and soluble materials introduced through condenser tube leaks.
- Oils and greases used during equipment maintenance and repair.
- Impurities not removed by makeup water treatment.
- Oxygen, nitrogen, and carbon dioxide contained in makeup water or auxiliary feedwater.
- Resin fines and beads from blowdown demineralizers, condensate polishers, or makeup water treatment systems.
- Chemicals used to regenerate resins, as well as trace impurities found in these chemicals.

There are numerous factors which affect corrosion product transport to the SGs, including:

- *Feedwater pH*: pH values in the range of 9.3 to 9.8 or greater are typically necessary to minimize iron transport to the SGs. However, pH values less than about 9.2 to 9.3 are typically necessary to maintain acceptably low copper concentrations if a plant contains copper in the secondary system. Plant-specific pH optimization is discussed in the EPRI PWR Secondary Water Chemistry Guidelines [20].

- *Condensate polishers*: Use of full flow condensate polishers can potentially reduce corrosion product transport by 30-50% for iron oxides, 75-90% for copper, and 20-50% for nickel [41]. However, since use of polishers generally requires operation of the plant with a lower than optimum feedwater pH in order to avoid rapid exhaustion of resins by the pH control amine, it is possible that operation without polishers at higher pH will result in a net reduction in overall corrosion product generation and transport.
- *Plant-specific piping arrangement*: The transport of corrosion products, especially particulates, is typically disproportionate between the SGs due to the specific inlet and outlet connection locations for different pipes and the resultant differences in flow patterns.
- *Plant transients*: Plant transients, including startup and shutdown, are of particular importance for corrosion product transport because operating conditions during plant transients may be substantially different than during normal operations. Therefore, material which was stable during normal operations may be released into the feedwater and transported to the SGs during transients. Additionally, exposure of secondary system surfaces to air or oxygenated water during outages can result in the generation of substantial amounts of corrosion products which are released and transported to the SGs during the subsequent startup.

Figure B-1 summarizes the overall process of deposit transport. Figure B-2 indicates typical sources of deposits and deposit precursors [1].

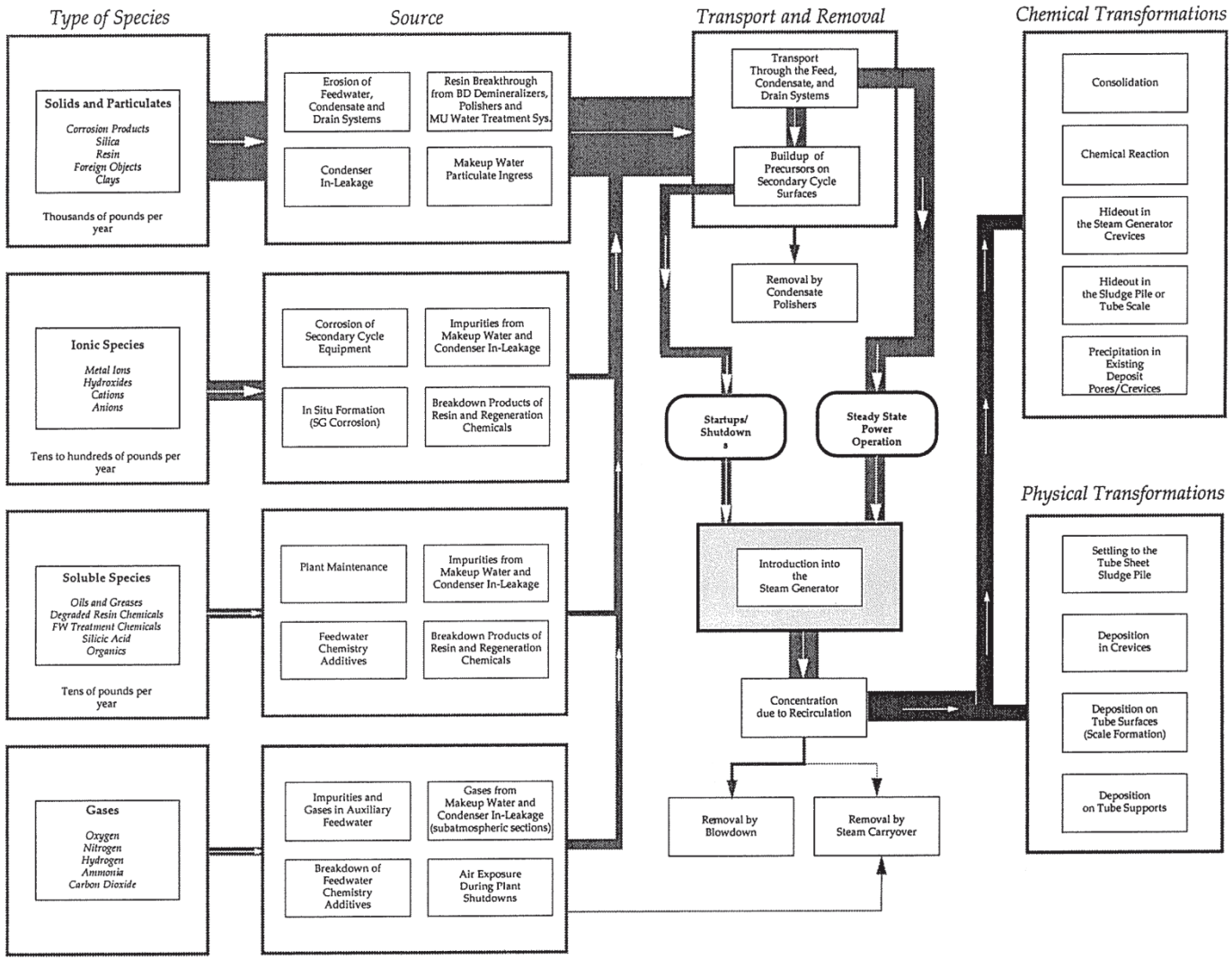

Figure B-1
Summary of Corrosion Product Generation and Transport [1]

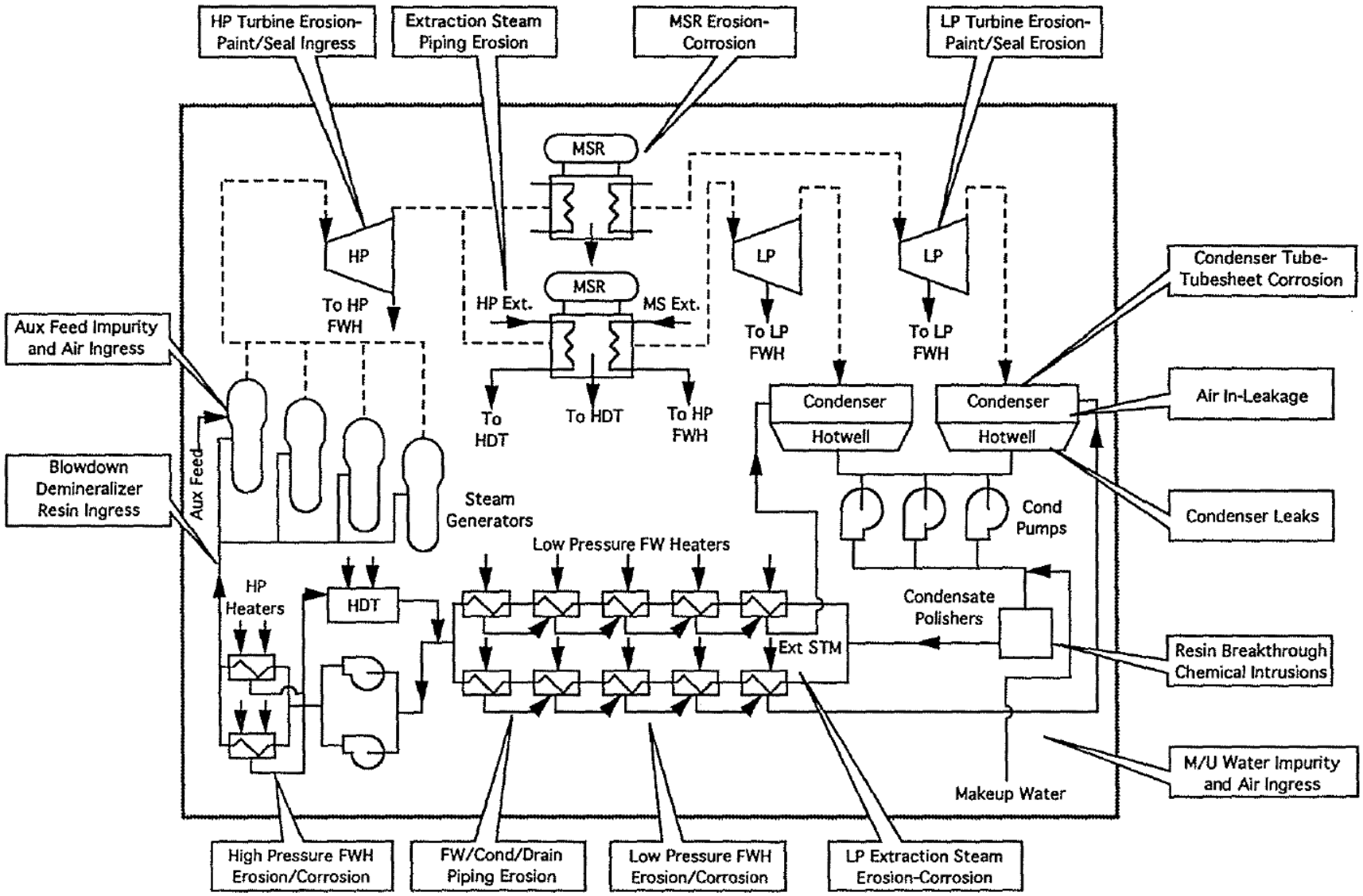

Figure B-2
Sources of Steam Generator Deposit Precursors [1]

B.2 Deposit Formation

Once in the SGs, corrosion products can be either: (1) removed by the blowdown system, (2) carried over with the steam, or (3) deposited on SG surfaces. In practice, removal via the blowdown has not been found to be an effective means of removing corrosion products from the SGs. Additionally, corrosion products carried over with the steam are transported to the condensers and thus may be transported to the SGs again. Therefore, the majority of corrosion products transported to the SGs are expected to ultimately end up as deposits on SG surfaces.

Formation of deposit precursors into deposits is thought to be governed by turbulent deposition, boiling deposition, gravitational settling, and re-entrainment:

- Turbulent deposition is the convection of particulate species to surfaces by the turbulent action of the fluid in the SGs, after which the species remain attached to the surface as a deposit. The particulate species are either carried into the SG from the feedwater or condensate system, or precipitated from dissolved chemical precursors within the SG.
- Boiling deposition is the concentration and precipitation of the deposit precursors due to evaporation of the feedwater on heat transfer surfaces (i.e., tube surfaces or existing deposits on tube surfaces).
- Gravitational settling is the transport of particulates to horizontal surfaces due to gravity. It is thought to be largely responsible for the formation of tube sheet sludge piles.
- Re-entrainment is the liberation of portions of existing deposits by mechanical action of the feedwater or by the vigorous hydraulic conditions associated with boiling.

The overall result of these factors is that the majority of deposits tend to accumulate on heat transfer surfaces (i.e., the tubes), and to a lesser extent in low flow regions (e.g., the top-of-the-tubesheet, or TTS). Flow velocity at the TTS is typically lowest at the centers of the hot and cold legs, leading to the formation of two distinct kidney-shaped deposit accumulations as shown in Figure B-3.

The exact mechanism of TTS collar formation is not fully understood, but is believed to be related to the presence of binding species such as aluminum and silicon. Analyses of TTS collars suggest that they tend to consolidate relatively quickly after forming (i.e., even relatively small or newly grown collars tend to have little to no porosity) [6].

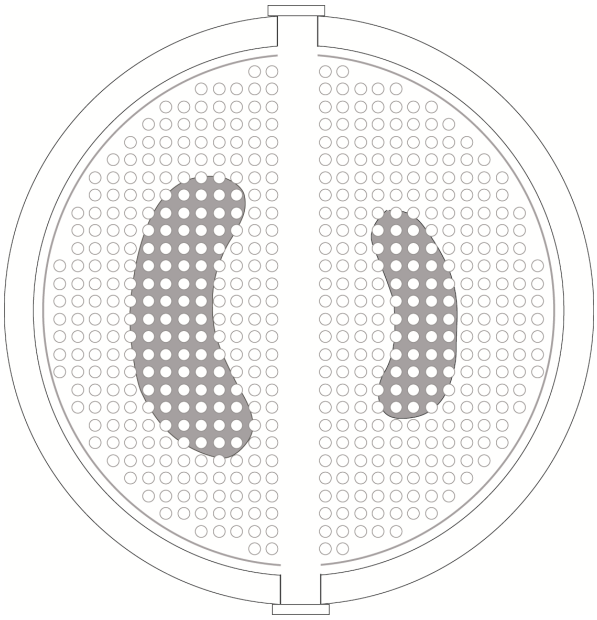

Figure B-3
Typical Kidney-Shaped Tubesheet Sludge Pile Regions [1]

Several design factors affect the exact distribution of deposits within the SGs, including:

- *Flow distribution baffles (FDBs)*: Flow distribution baffles were included in some SG designs in an attempt to increase cross flow velocities at the TTS and thereby reduce sludge pile formation. In practice, FDBs have not led to a substantial reduction in sludge pile formation. Some plants with FDBs have reported sludge accumulation on top of the FDB and/or sludge piles located at the overall center of the tube bundle rather than in the centers of the hot and cold legs (as shown in Figure B-3).
- *Preheater*: The presence of a preheater on the cold leg increases the cross flow velocity on the cold leg, leading to the preferential accumulation of deposits on the hot leg. Some plants have also reported deposit formation on the preheater baffles.
- *Stay cylinders*: As with FDBs and preheaters, stay cylinders affect the flow patterns at the TTS, changing deposit locations. Stay cylinders are thought to contribute to the fact that the initial deposit buildup occurs in the upper bundle and near the TTS for both legs in some CE SGs, rather than at the middle TSP elevations [5].
- *Tube support plate (TSP) design*: Different TSP designs can also lead to differences in the manner in which deposits accumulate, and associated concerns. In older SGs with drilled hole TSPs, deposits tend to fill the crevice formed between the SG tube and TSP. In the past, this phenomenon has led to TSP denting at units with carbon steel TSPs. In newer SGs with more open TSP designs (e.g., quatrefoil, trefoil, and eggcrate/lattice designs), deposits can accumulate in flow passages (e.g., quatrefoil lobes) and disrupt normal flow patterns, leading to vibration-related tubing failures and/or level oscillations [2, 3]. The most significant deposition and TSP blockage is typically observed at the upper TSP elevations, where the steam quality is the highest.

C
NATURE OF STEAM GENERATOR DEPOSITS

The purpose of this chapter is to briefly review the nature of steam generator deposits. Additional information on this topic can be found in References [1] and [6], as well as in the references reviewed in Section 5.2.

C.1 Chemistry of Key SG Deposit Species

Over 150 chemical compounds have been identified in deposits found in the SGs and connected systems (feedwater, steam and condensate) [42]. An extensive list of constituents that may be found in SG deposits is provided in Table C-1. The remainder of this section discusses the typical chemistry of the most common and important deposit species.

Table C-1
Summary of Candidate Deposit Constituents (Adapted from Reference [1])

Element (Symbol)	Potential Deposit Species	Formula	Molecular Weight	Color	Density	Melting Point °C
Aluminum (Al)	γ-Alumina (Corundum)	$\gamma\text{-}Al_2O_3$	101.96	Colorless	3.97	Transforms to $\alpha\text{-}Al_2O_3$
	Boehmite	AlO(OH)	59.99	White	3.01	Transforms to $\gamma\text{-}Al_2O_3$
	Diaspore	AlO(OH)	59.99	Colorless	3.40	Transforms to $\alpha\text{-}Al_2O_3$
	α-Alumina	$\alpha\text{-}Al_2O_3$	101.96	White	3.97	2980
	Gibbsite	$Al_2O_3 \bullet 3H_2O$	156.01	White	2.42	Transforms to $\gamma\text{-}Al_2O_3$ (T < 300°C)
	Bayerite	$Al_2O_3 \bullet 3H_2O$	156.01	White	2.53	Transforms to $\gamma\text{-}Al_2O_3$ (T < 300°C)
	Cyanite	$Al_2O_3 \bullet SiO_2$	162.04	White	3.25	1545
	Mullite	$3Al_2O_3 \bullet SiO_2$	426.05	Colorless	3.16	1920
	Brindleyite	$(Ni_2Al)(Al,Si)O_5(OH)_4$	Varies	-	-	-
	Pyrophyllite	$Al_2Si_4O_{10}(OH)_2$	360.31	-	-	-
	Kaolinite	$Al_2Si_2O_5(OH)_4$	258.16	-	-	-
	Albite	$NaAlSi_3O_8$	262.22	-	-	-
	Nepheline	$NaAlSiO_4$	142.05	-	-	-
Arsenic (As)	Arsenolite	As_2O_3 (or As_4O_6)	197.84	Colorless	3.74	193 (dissociates)
	Claudetite	As_2O_3 (or As_4O_6)	197.84	Colorless	4.20	193 (dissociates)
	None	$Ni_{11}As_8$	1244.95	-	-	-
	None	AsNiS	165.67	-	-	-
	Realgar (Orpiment)	As_2S_3	213.97	Red-Brown	3.51	595
	Niccolite	NiAs	133.63	-	7.57	968
Barium (Ba)	Barium Oxide	BaO	153.34	Colorless	5.72	1918
	Barite	$BaSO_4$	233.40	White	4.50	1580
Boron (B)	Oxide Glass	B_2O_3	69.62	Colorless	1.81	450
	Boric Acid	H_3BO_3	61.83	Colorless	1.44	169
	Metaboric Acid	HBO_2	43.82	White	2.49	236
Cadmium (Cd)	Cadmium Oxide	CdO	128.40	Brown	8.15	1500
	Greenockite	CdS	144.46	Yellow	4.82	1750
Calcium (Ca)	Lime	CaO	56.08	Colorless	3.25	2614
	Truscottite	$Ca_{14}Si_{24}O_{58}(OH)_8 \bullet 2H_2O$	-	-	-	-
	Calcite (Aragonite)	$CaCO_3$	100.09	Colorless	2.71	1339
	Celite	$4CaO \bullet Fe_2O_3 \bullet Al_2O_3$	485.97	Brown	3.77	1418
	Diopside	$CaO \bullet MgO \bullet 2SiO_2$	216.56	Colorless	3.28	1391
	Whitlockite	$Ca_3(PO_4)_2$	310.18	White	3.14	1670
	Hydroxylapatite	$Ca_5(PO_4)_3OH$	502.31	White	-	-
	Anhydrite	$CaSO_4$	136.14	Colorless	2.96	1450
	Alite	Ca_3SiO_5	228.32	Colorless	-	1900
	Wollastonite	$CaSiO_3$	116.16	Colorless	2.91	1540
	Pekovskite	$CaTiO_3$	135.98	Colorless	4.10	1975
	Calcium Silicate	$Ca_3Si_2O_7$	288.41	Colorless	-	-
Chromium (Cr)	Chromium Oxide	Cr_2O_3	151.99	Green	5.21	2266
	Silicide	Cr_3Si_2	212.17	Gray	5.50	-
Cobalt (Co)	Cobalt Oxide	Co_2O_3	165.86	Black-Gray	5.18	895
Copper (Cu)	Copper Metal	Cu	63.55	Orange-Red	8.92	1083
	Nantokite	CuCl	98.99	White	4.14	430
	Cuprite	Cu_2O	143.08	Red	6.00	1235
	Tenorite	CuO	79.54	Black	6.35	1326
	None	Cu_4Si	282.25	White	7.53	850
	Brochantite	$CuSO_4 \bullet 3Cu(OH)_2$	452.27	Green	3.78	300
	Chalcocite	Cu_2S	159.14	Black	5.60	1100

Table C-2 (continued)
Summary of Candidate Deposit Constituents (Adapted from Reference [1])

Element (Symbol)	Potential Deposit Species	Formula	Molecular Weight	Color	Density	Melting Point °C
Iron (Fe)	Magnetite	Fe_3O_4	231.54	Black	5.18	1594
	Maghemite	γ-Fe_2O_3	159.69	Brown-Red	4.87	-
	Hematite	α-Fe_2O_3	159.69	Red	5.24	1565
	Lepidocrocite	γ-FeOOH	88.85	Orange	4.09	-
	Goethite	α-FeOOH	88.85	Yellow	4.28	136
	Iron Arsenide	FeAs	130.77	White	7.83	1020
	Arsenoferrite	$FeAs_2$	205.69	Silver-Gray	7.40	990
	Iron Chromite	$FeCr_2O_4$	223.84	Brown	4.97	-
	Maricite	$NaFePO_4$	173.80	Gray	-	-
	Gruenerite	$FeSiO_3$	131.98	Gray-Green	3.50	1146
	Fayalite	Fe_2SiO_4	203.78	Gray	4.34	1503
	Marcasite	FeS_2	119.98	Yellow	4.87	450
	Troilite	FeS	87.91	Black-Brown	4.74	1193
	Iron Oxide Spinel	$Fe_2Cr_2(Ni,Mn,Zn)O_4$	-	Black-Brown	-	-
Lead (Pb)	Litharge	PbO	223.19	Yellow	9.53	886
	Hydrocenssite	$2PbCO_3 \bullet Pb(OH)_2$	775.60	White	6.14	400
	Cerussite	$PbCO_3$	267.20	Colorless	6.60	315
	Cotunnite	$PbCl_2$	278.10	White	5.85	501
	Crocoite	$PbCrO_4$	323.18	Yellow	6.12	844
	Wulfenite	$PbMoO_4$	367.13	Light Yellow	6.92	1060
	Plattnerite	PbO_2	239.19	Bronze	9.38	290
	Massicot	PbO	223.19	Yellow	8.00	-
	Minium	Pb_3O_4	685.57	Red	9.10	500
	Matlockite	$PbCl_2 \bullet Pb(OH)_2$	519.29	White	7.21	524
	Mendipite	$PbCl_2 \bullet 2PbO$	724.47	Yellow	7.08	693
	Alamosite	$PbSiO_3$	283.27	Colorless	6.49	766
	Barysilite	$Pb_2Si_2O_7$	582.55	White	6.71	-
	Anglesite	$PbSO_4$	303.25	White	6.20	1170
	Lanarkite	$PbSO_4 \bullet PbO$	526.44	White	6.92	977
	Galena	PbS	239.25	Blue	7.50	1114
	Metatitanate	$PbTiO_3$	303.09	Yellow	7.52	-
Lithium (Li)	Lithium Hydroxide	LiOH	23.95	White	1.46	450
	Aluminate	$LiAlO_2$	65.92	White	2.55	1900
	Lithium Sulfate	Li_2SO_4	109.94	-	2.22	845
Magnesium (Mg)	Periclase	MgO	40.31	Colorless	3.58	2852
	Spinel	$MgAl_2O_4$	142.27	Colorless	3.60	2135
	Ascharite	$Mg_2B_2O_4 \bullet H_2O$	168.26	-	2.60	-
	Pinnoite	$Mg(BO_2)_2 \bullet 3H_2O$	163.98	Yellow	2.27	-
	Magnesite	$MgCO_3$	84.32	White	2.96	350
	Sellaite	MgF_2	62.31	Colorless	-	1261
	Orthophosphate	$Mg_3(PO_4)_2$	262.88	Irridescent	-	1184
	Pyrophosphate	$Mg_2P_2O_7$	222.57	Colorless	2.56	1383
	Clinoenstatite	$MgSiO_3$	100.40	White	3.19	1557
	Forsterite	Mg_2SiO_4	140.71	White	3.21	1910
	Serpentine	$Mg_3Si_2O_5(OH)_4$	277.09	White	2.55	-
	Nimite	$Mg_6(Si,Al)_4O_{10}(OH)_8$	-	-	-	-
	Chinchlore	$(Mg,Fe)_6(Si,Al)_4O_{10}(OH)_8$	-	-	-	-

Table C-3 (continued)
Summary of Candidate Deposit Constituents (Adapted from Reference [1])

Element (Symbol)	Potential Deposit Species	Formula	Molecular Weight	Color	Density	Melting Point °C
Manganese (Mn)	Maganosite	MnO	70.94	Green	5.44	-
	Arsenide	MnAs	129.86	Black	6.17	400
	Pyrochroite	$Mn(OH)_2$	88.95	White-Pink	3.26	Dissociates at T < 300°C
	Magnanite	MnO(OH)	87.94	Brown-Black	4.2 - 4.4	Dissociates at T < 300°C
	Hausmannite	Mn_3O_4	228.81	Black	4.85	1564
	Pyrolusite	MnO_2	86.94	Black	5.03	535
	Braunite	Mn_2O_3	157.87	Black	4.50	1080
	Reddingite	$Mn_3(PO_4)_2$	408.80	Rose	3.10	-
	Rhodonite	$MnSiO_3$	131.02	Red	3.72	1323
	Pyrophanite	$MnTiO_3$	150.84	Yellow	4.54	1360
Mercury (Hg)	Montroydite	HgO	216.59	Yellow-Red	11.10	500
	Calomel	Hg_2Cl_2	472.09	White	7.15	400
	Cinnabar	HgS	232.65	Red	8.10	583
Molybdenum (Mo)	Molybdite	MoO_3	143.94	White-Yellow	4.69	795
	Molybdenite	MoS_2	160.07	Black	4.80	1185
Nickel (Ni)	Bunsenite	NiO	74.71	Green-Black	6.67	1984
	Breithauptite	NiSb	180.46	Copper	7.54	1158
	Niccolite	NiAs	133.63	Black	7.57	968
	Millerite	NiS	90.77	Black	5.30	797
	Heazlewoodite	Ni_3S_2	240.26	Yellow	5.82	790
	Poydomite	Ni_3S_4	304.39	Gray	4.70	-
	Nickel Ferrite	$Ni_{0.3}Fe_{2.7}O_4$	232.39	Black	-	-
Phosphorous (P)	Phosphorous Pentaoxide	P_2O_5	141.94	Colorless	2.14	23.8
	Phosphorous Sulfide	P_2S_5	222.27	Grey-Yellow	2.03	290
Potassium (K)	Potassium	K	39.10	-	-	-
	Kaluszite	$K_2Ca(SO_4)_2H_2O$	328.42	Colorless	2.60	1004
	Langbelinite	$K_2SO_4 \bullet 2MgSO_4$	415.01	-	2.83	927
Antimony (Sb)	Senarmontite	Sb_2O_3	291.50	White	5.20	656
	Cervantite	Sb_2O_4	307.50	White	5.82	930
	Stibnite	Sb_2S_3	339.69	Black	4.64	550
Sodium (Na)	Oxide Glass	Na_2O	61.98	White-Gray	2.27	1275
	Albite	$NaAlSi_3O_8$	262.22	Colorless	2.61	1100
	Jadeite	$Na_2O \bullet Al_2O_3 \bullet 4SIO_2$	404.28	Colorless	3.30	1000
	Nephelite	$Na_2O \bullet Al_2O_3 \bullet 2SIO_2$	284.11	Colorless	2.61	1526
Sulfur (S)	Included primarily as sulfates with other elements in this table.					
Tin (Sn)	Cassiterite	SnO_2	150.69	White	6.95	1630
	Mosaic Gold	SnS_2	182.82	Golden	4.50	600
Silver (Ag)	Silver Oxide	Ag_2O	231.74	Brown	7.14	230
	Argentite	Ag_2S	247.80	Black	7.32	825
Titanium (Ti)	Octahedrite	TiO_2	79.90	Brown	3.84	-
	Brookite	TiO_2	79.90	White	4.17	1825
	Rutile	TiO_2	79.90	Colorless	4.26	1830
Silicon (Si)	Cristobalite	SiO_2	60.08	Colorless	2.32	1723
	Lechatelierite	SiO_2	60.08	Colorless	2.19	2230
	Quartz	SiO_2	60.08	Colorless	2.63	1610
	Opal	$SiO_2 \bullet xH_2O$	-	Colorless	2.17	1600
	Tridymite	SiO_2	60.08	Colorless	2.26	1703
Zinc (Zn)	Zincite	ZnO	81.37	White	5.61	1975
	Gahnite	$ZnAl_2O_4$	183.33	Green	4.58	-
	Ferrite	$ZnFe_2O_3$	241.06	Black	5.33	1590
	Hemimorphite	$2ZnO \bullet SiO_2 \bullet H_2O$	240.84	Colorless	3.45	-
	Willemite	Zn_2SiO_4	222.82	-	4.10	1509
	Wurtzite	ZnS	97.43	Colorless	3.98	1700
	Sphalerite	ZnS	97.43	Colorless	4.10	1020

C.1.1 Iron

The main constituent of most PWR secondary side deposits is iron oxide. Although typically found in the form of magnetite, iron can also be found in the more oxidized forms such as hematite and maghemite, and as iron hydroxides and oxyhydroxides. Additionally, several other common elements (e.g., nickel, chromium, zinc, etc.) are known to form non-stoichiometric ferrites (also referred to as substituted-spinels). The presence of these spinels is typically confirmed during deposit characterization studies when local analysis by energy dispersive spectroscopy (EDS) identify co-located inclusions containing both iron and nickel (and/or one of the other species mentioned above), and XRD shows that the secondary species (nickel, etc.) is not present as a phase that can be distinguished from magnetite (see additional discussion in Section 3.2.4.2).

While magnetite alone is not believed to be corrosive to SG materials, it has been reported that it may reduce sulfates to sulfides (which have been associated with tube corrosion) [43]. It has also been reported that magnetite may catalyze the decomposition of morpholine into acetates and the decomposition of oxygen scavengers such as hydrazine [44, 23]. Finally, magnetite dissolution in acidic environments is believed to lead to a lower pH_T limit of 3.5 for solutions in contact with deposits [45].

C.1.2 Nickel

Nickel, which is present at low levels in carbon steel throughout the secondary system and at high levels in the SG tubes and some other secondary side heat exchanger tubes, is often found as the substituted-spinel nickel ferrite, $Fe_{3-x}Ni_xO_4$ (where x is limited between 0 and 1 due to the fact that nickel only exhibits the +2 oxidation state). Once formed, it is unlikely that nickel ferrite will be reduced to magnetite and nickel oxide (NiO) [46]. Additionally, the presence of nickel ferrite can lead to slower deposit dissolution kinetics in SG chemical cleaning solutions [47].

Nickel can also form nickel sulfide (NiS_2), which has been linked to sulfur-induced corrosion [44].

C.1.3 Copper

Historically, copper was often used in heat exchanger tubing in balance-of-plant (BOP) systems (e.g., condenser, feedwater heaters, etc.) due to its excellent heat transfer properties, low cost, and use in other industries. However, copper oxide was found to accelerate stress corrosion cracking and denting [58] of SG tubing. Therefore, many utilities have opted to replace copper bearing alloys with copper-free materials such as stainless steel or titanium. Despite these copper minimization efforts, other sources of copper exist. For example, carbon steel can contain up to 0.4% tramp copper, and even nominally “copper-free” plants typically have low levels of copper in their SG deposits (typically on the order of 0.1%). Plants with copper alloys present in BOP systems typically have 5-20 wt% copper in their SG deposits, although levels up to about 50 wt% have been observed.

Copper is typically found as an inclusion of copper metal within SG deposits [1]. However, copper present in SG deposits may be oxidized during refueling outages when deposits are exposed to air during maintenance activities [22, 23]. The presence of copper oxides is expected to raise the electrochemical potential near the SG tubes significantly, and has been linked to

numerous corrosion phenomena, including pitting and SCC of SG tubing [20]. Thus, it is important to maintain strongly reducing conditions during startup evolutions to ensure that any copper oxides are converted back to copper metal prior to normal operation at high temperature [22, 23].

C.1.4 Aluminum, Silicon, and Hardness Species

Although generally present at relatively low concentrations within SG deposits, aluminum, silicon, and other hardness species are believed to play an important role in the initial formation of deposits. Additionally, higher aluminum-to-silicon ratios in SG deposits have been shown to correlate with earlier occurrences of SCC at plants with Alloy 600MA SG tubing [48].

Tube scale flakes typically contain on the order of 1 wt% aluminum compounds and 1 wt% silicon compounds, while TTS collars typically contain 25-35 wt% aluminum compounds and 5-10% silicon compounds [15]. As indicated in Table C-1, hardness species can form numerous different chemical compounds. Further, unlike with magnetite and substituted-spinels, no one compound form has been found to be prevalent in SG deposits. In fact, multiple different compound forms of aluminum and silicon are often found within a single TTS collar [6].

C.1.5 Lead

While lead concentrations in secondary side deposits are low (typical on the order of 100 to 1000 ppm), it is typically a species of interest in deposit characterizations due to the fact that lead has been shown to accelerate SCC of 600MA, 600SR, 600TT, 690TT, and 800NG in laboratory tests [1, 20]. Further, higher lead concentrations in tube scale flakes have been shown to correlate with earlier occurrences of SCC at plants with Alloy 600MA SG tubing [48].

Numerous potential sources of lead have been identified, including (alphabetically) [1]:

- Babbitt alloys
- Brazes and solders
- Condenser leaks
- Copper alloys (including Muntz metals)
- Greases, lubricants, and graphite cutting oils
- Lead chromate tinting in polyethylene wrapping materials
- Marking pencils
- Metallic lead particles from turbine positioning wires, lead hammers, and lead shielding blocks/blankets
- Plant makeup water (primarily where sources are polluted)
- Preservatives, paints, and coatings (e.g., turbine paints/coatings at Kori and St. Lucie)

- Seals, bearings, and gaskets (e.g., turbine rupture disc seal rings)
- Secondary side conditioning systems (e.g., morpholine, hydrazine, and ammonia, which have trace amounts but are used in significant quantity)
- Valve packing materials

C.1.6 Sulfur

Sulfur is another species that, although present in low concentrations in deposits (typically 10 to 100 ppm), is often of interest in deposit characterizations due to its potential to cause SG tubing degradation. Additionally, it is often found at concentrations up to two orders of magnitude higher near or within tube cracks [1]. While sulfate has been associated with IGA/SCC due to pH effects and with wastage, reduced sulfur has been associated with more severe, species-specific corrosion mechanisms including intergranular attack (IGA), pitting, and stress corrosion cracking (SCC) [20].

Numerous potential sources of sulfur have been identified, including (alphabetically) [1, 20]:

- Chemical cleaning solution residuals (when rinsing is not adequately performed following SG chemical cleaning operations)
- Condenser leaks
- Makeup water and improper regeneration of resins in makeup demineralizers and condensate polishers
- Resin ingress from demineralizers, condensate polishers, or blowdown regenerative cleanup systems
- Thermal degradation of oils and other chemicals

C.2 SG Deposit Types

As discussed in Section B.2, deposits tend to form on the surface of the SG tubes or on horizontal surfaces such as the TTS and TSPs. As deposits that form in similar locations tend to share similar characteristics, it is useful to discuss several characteristic types of deposits, including:

- Tube scale
- TSP blockages
- TTS collars (sometimes referred to as “hard sludge”)
- Loose powdered sludge (sometimes referred to as “soft sludge”)
- Other material (e.g., debris, loose parts)

All of these deposits types are discussed briefly in Section 3.1.3, with the exception TSP blockage deposits which generally are not found intact in SG deposit samples. These deposit types illustrated in Figure C-4, Figure C-5, and Figure C-6, and are discussed in more detail below.

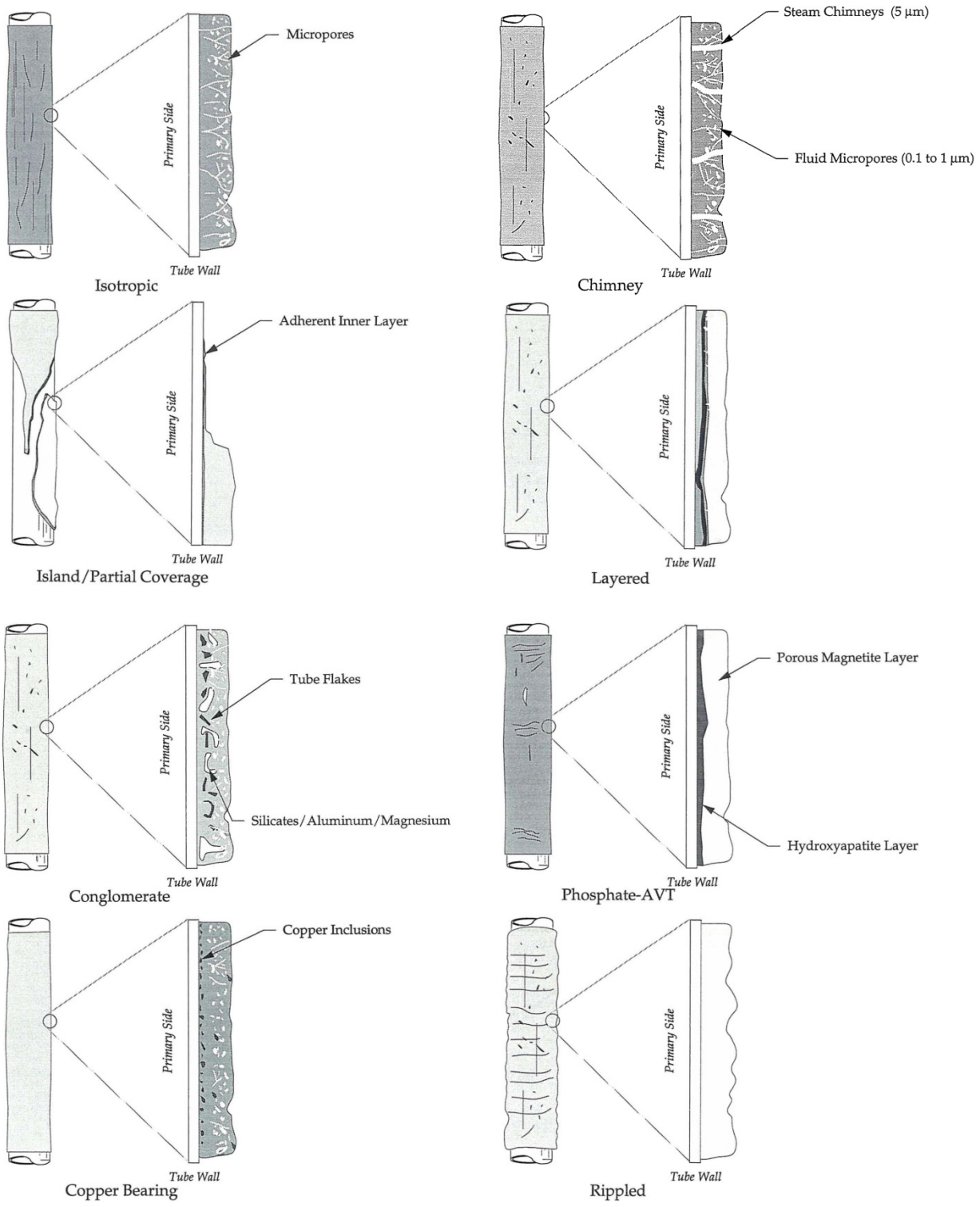

Figure C-1
Characteristics of Tube Scale Types [1]

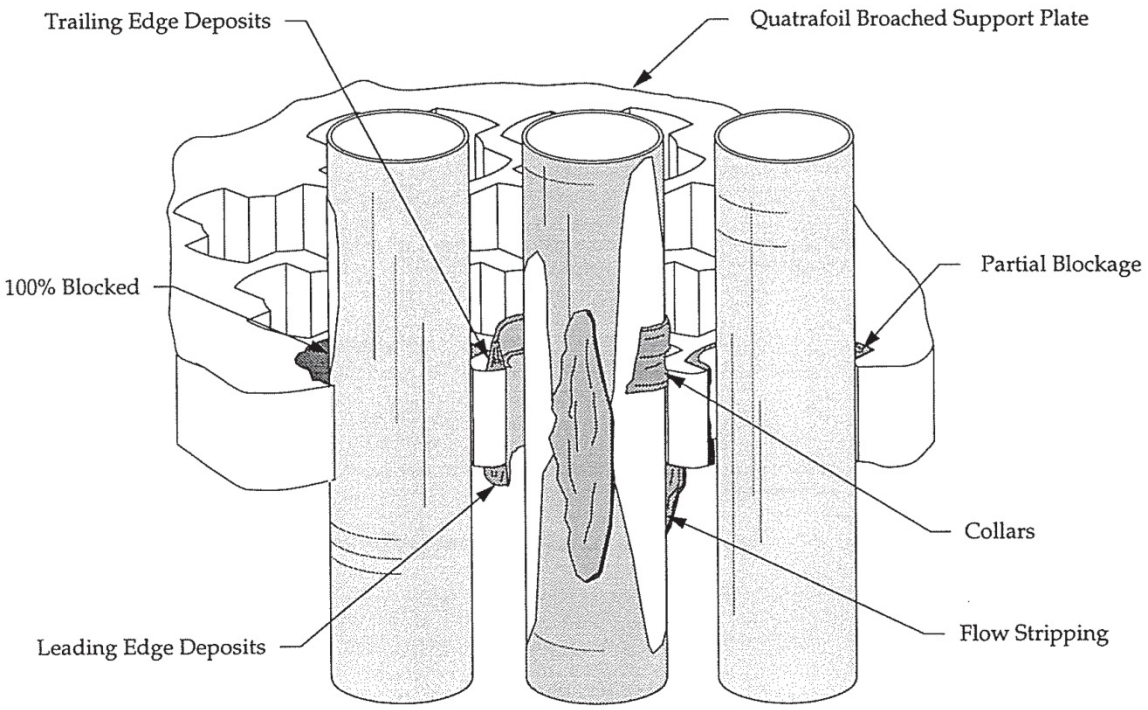

Figure C-2
Illustration of TSP Blockages [1]

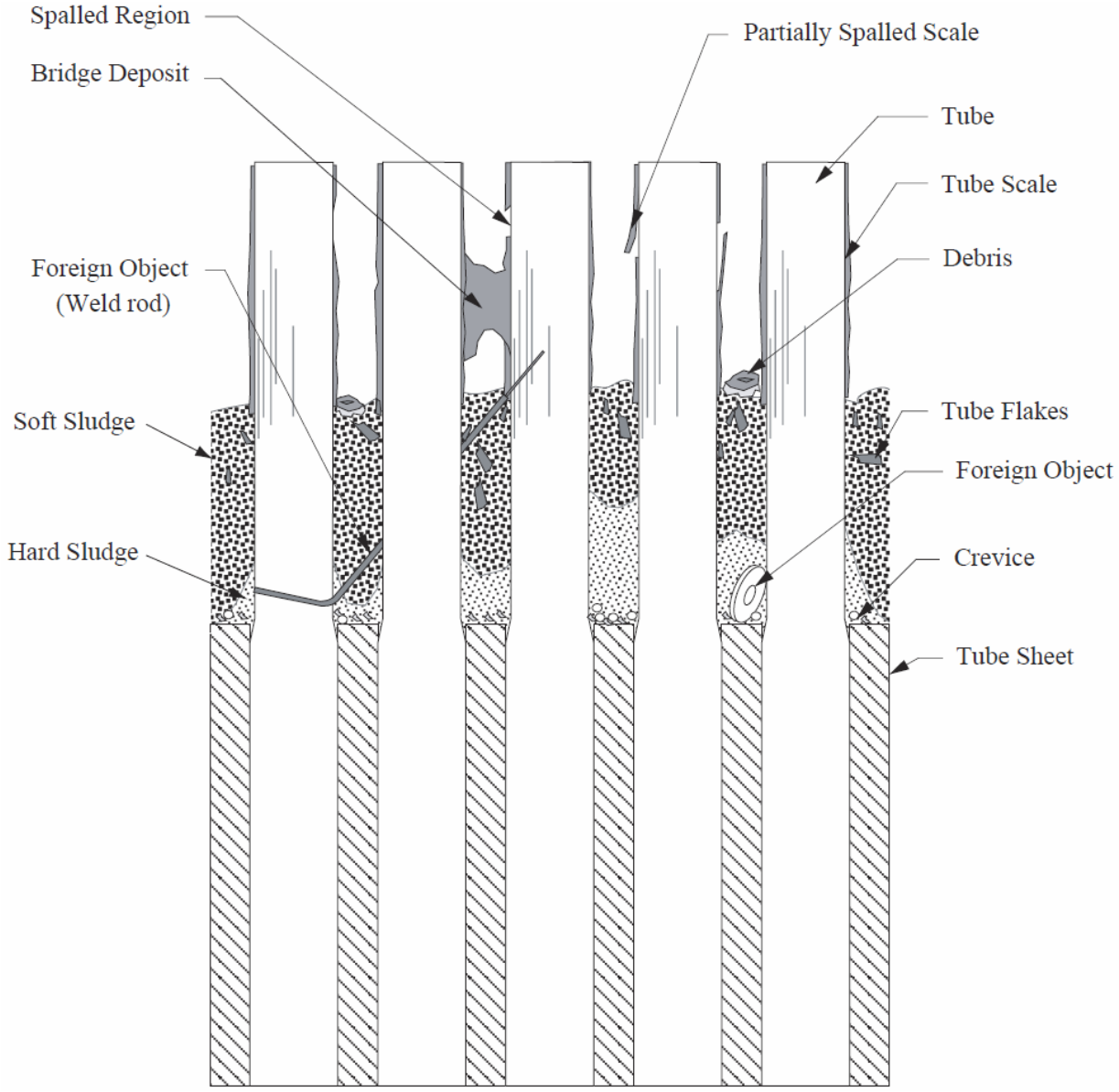

Figure C-3
Characteristics of a Tubesheet Sludge Pile (Adapted from Reference [1])

C.2.1 Tube Scale

Tube scale typically accounts for a majority of the overall deposit mass present in PWR SGs. Tube scale is a type of deposit which forms on heat transfer surfaces as a result of chemical processes (involving crystallization from solutions) and/or physical processes (involving adhesion of particulates to the tube surface). The mechanisms for tube scale formation are discussed in more detail in Reference [1]. Different types of tube scale and different tube scale characteristics are shown in Figure C-4 and are reviewed below.

C.2.1.1 Isotropic Scale

Isotropic deposits exhibit a uniform porous structure and are almost always found in plants that operate with AVT chemistry and do not have copper bearing materials in their secondary cycle. They are usually composed almost entirely of magnetite, but often contain preferential concentrations of thin layers of nickel, chromium, and/or aluminum species directly at the scale to tube interface. Secondary side visual inspections of plants with such deposits often show generally uniform surface coverage throughout the tube bundle, with some SGs appearing to have thicker scale higher in the tube bundle (although variations in scale thickness at different elevations and in the two legs are common, and thicker scale may be observed in other locations). Isotropic tube scale typically has a porosity of 10–30%.

C.2.1.2 Wicks and Chimneys

Tube scale contains a large number of small capillaries or micropores (typically about 0.3 μm / 0.01 mil in diameter) called *wicks* and larger pores (typically 5 to 20 μm / 0.2 to 0.8 mil in diameter) called *chimneys* in the scale structure. The chimneys are thought to provide the main route for escaping steam produced by boiling close to the tube wall, with 10 μm (0.4 mil) chimneys having been suggested as providing optimal heat transfer benefit. The optimum chimney population for heat transfer (measured in terms of surface terminations per unit of scale surface area) has been suggested to be about 5,000 chimneys per mm^2 (3.2 chimneys per mil^2) [49]. The wicks, also called micropores or capillaries, are thought to supply liquid water to the base of chimneys. The surface population of these wicks is about $2.5x10^6$ wicks per mm^2 (1,600 wicks per mil^2). This means that, for optimum heat transfer, the fraction of the surface area occupied by the wicks and the chimneys should be about equal.

In addition to promoting heat transfer, wicks and chimneys may promote the concentration of impurities close to the tube surface. The combined heat and mass transfer in deposits with wicks and chimneys has been studied extensively, and concentration factors have been estimated to be as low as 4 to as high as 1000 [50, 51, 52].

C.2.1.3 Island/Partial Coverage

Island/partial coverage occurs as a result of partial spalling or exfoliation of the outer layer of the tube scale, leaving behind a thinner, more adherent layer (see Figure C-4). Spalling/exfoliation is the process of tube flakes breaking away from the tubing surface. (As discussed above, these tube scale flakes may be later collected in deposit samples obtained during sludge lancing.) In nuclear SGs, it is believed that the thermal expansion and contraction of tubing during temperature transients (e.g., startup and shutdown) and the relatively high flow velocity during normal operations play an important role in tube scale spalling. In contrast, minimal tube scale spalling is believed to occur during operations that result in relatively low flow velocities within the SGs (e.g., drain/refill operations) [6]. It is also thought that spalling may occur preferentially along the boundary between two different scale layers (see discussion of layered scale, in Section C.2.1.4).

C.2.1.4 Layered Scale

Tube scale is often found to consist of several distinct compositional and structural layers (see Figure C-4) [53]. Ostensibly, the composition and structure of each layer may be related to events in the life of the plants, such as changes in feedwater treatment chemicals, impurity ingresses, or changes in secondary cycle equipment (e.g., replacement of copper bearing alloys). For example, tube scale may exhibit a very dense inner layer, but a very porous outer layer. These sub-layers are thought to form continuously throughout plant life and occasionally exfoliate (especially during transients), and are important for both short-term and long-term trends in SG thermal performance.

C.2.1.5 Conglomerated Deposits

Conglomerated deposits are an amalgamation of insoluble material, compound phases, metallic inclusions, debris, and in some cases, even exfoliated tube flakes. They are particularly non-homogeneous and have little to no porosity. Conglomerated deposits most commonly form at the tubesheet and are referred to as TTS "collars" (see additional discussion in Section C.2.4). However, conglomerated structure can also be observed in thicker tube scales and at TSP elevations.

C.2.1.6 Phosphate/AVT Scale

Phosphate/AVT scale is a particular type of layered scale associated with plants that began operation on phosphate feedwater treatment regimes and later switched to all volatile treatment (AVT). This sequence tends to result in tube scale that exhibits a distinct two-layered structure. In one study, the inner layer was found to contain primarily a dense calcium hydroxylapatite material ($Ca_5(PO_4)_3OH$), a hydrated form of calcium phosphate that is believed to have formed under phosphate water treatment [54]. The outermost layer is more typical of an isotropic deposit, e.g., primarily magnetite with occasional local inclusions of copper and dispersed nickel, chromium, and hardness elements.

C.2.1.7 Copper Bearing Scale

Even for "copper free" plants, it is common to observed metallic copper inclusions within SG tube scale. Copper inclusions are generally evenly dispersed within the scale matrix, but some copper inclusions have been found preferentially in a certain portion of the scale (e.g., near the tube OD). Tube scale at plants with copper present in balance-of-plant (BOP) systems is characterized by much higher concentrations of copper inclusions.

C.2.1.8 Rippled Scale

Rippled scale exhibit bands or waves over its outer surface, and has been seen in numerous SGs. The height of ripples on the surfaces of such deposits may be about a factor of 2 higher than that of the average thickness of the scale [55].

One of the interesting effects of rippled scale in SGs is that it may increase heat transfer efficiency [56]. Specifically, smooth deposits have been found to exhibit a friction factor of 0.018 to 0.02, while the friction factor for rippled deposits is greater, perhaps 0.025 to 0.04 [55]. As a result, single phase heat transfer, which is approximately linearly dependent on friction factor at high Reynolds numbers, may increase by up to a factor of about two when rippled deposits are present.

C.2.2 TSP Blockages

TSP blockages are the deposits which form at the intersections of the tubes and the tube supports, and result in clogging of TSP flow passages. These deposits disrupt normal flow patterns and can result in undesirable side effects such as vibration-induced wear and water level instabilities.

The TSP material of construction has been shown to impact the extent of deposit formation. For example, austenitic materials have been shown to be less prone to the formation of deposits than ferritic stainless steels, which are in turn are much less prone to deposit formation than carbon or low alloy steel.

C.2.3 Loose Powdered Deposits

Loose powder deposits, also referred to as *soft sludge*, are highly mobile, silt-like deposits which accumulate in low flow areas. Loose powder deposits may enter the SG as particulates and settle to the TTS, form in the SG due to the concentration and precipitation of soluble species, or form in the SG due to pulverization of other deposit types (e.g., SG tube scale) during normal operation or maintenance activities.

The main constituents of loose powder are typically magnetite (usually >70% at copper-bearing plants and >90% at copper-free plants) and copper (typically <1% at copper-free plants and typically 5-20% at copper-bearing plants). Other components (e.g., zinc, nickel, silicon, calcium, manganese, aluminum, etc.) may also be present at low levels (typically several percent or less). The bulk and skeletal densities of loose powder deposits are typically around 1-2 g/cm^3 and 5-6 g/cm^3, respectively, and the specific surface area is typically in the range of 3-6 m^2/g [1].

C.2.4 Consolidated TTS Collars

Consolidated TTS collars, also referred to as *hard sludge* or just *collars*, are highly consolidated deposits which form at the tube-to-tubesheet intersection. As with soft sludge, collars tend to form preferentially in low flow areas.

TTS collars are highly heterogeneous, typically consisting of one or more main phases (e.g., aluminosilicates, etc.) acting as a binding agent which holds together numerous inclusions of other materials (e.g., magnetite, copper, metallic debris, etc.). Relative to other deposits in SGs, TTS collars contain significantly higher concentrations of aluminum and silicon. Based on compositional analysis of over 50 collars from about 25 plants, TTS collars contain on average about 40-50% iron oxide, 25-35% aluminum oxides, 5-10% silicon oxides, 5-10% copper, and lesser amounts of numerous other species (e.g., zinc, nickel, chromium, calcium, manganese, lead, etc.). The standard deviations associated with these concentration ranges are about 20% for iron and aluminum oxides and about 5-10% silicon oxide and copper [6, 15].

The porosity of the TTS collars is typically less than about 1%, which suggests that, unlike tube scale which is thought to gradually densify over time, TTS collars tend to consolidate rapidly or form with little to no porosity [6]. The low porosity of TTS collars also indicates that the crevice underneath the collar is highly occluded and unlikely to have significant interaction with the bulk fluid during normal operation. Thus, even small TTS collars tend to insulate the underlying crevices, leading to elevated temperatures within the crevices (within about 5°C or 9°F of the local primary side temperature) and potentially aggressive crevice environments. As such, ongoing TTS maintenance is necessary to reduce the inventory of TTS sludge and minimize the risk of tubing degradation [5, 6, 15].

C.2.5 Other Materials Found in SGs

While the characteristic deposit types discussed above typically account for the majority of the deposits in a SG, other materials can be found. These include:

- Deposits which formed elsewhere in the secondary circuit (e.g., in the feedwater system) and which subsequently spalled off and were transported to SGs,
- Hard consolidated deposits which bridge intertube gaps between support plates or in U-bends (*bridge deposits*, see Figure C-6),
- Tube collars above or below tube support plates, also known as rings to differentiate formation at a TSP versus the TTS (*collars*, see Figure C-5),
- Remnants of phosphate sludge (in SGs operated with phosphate-based feedwater chemistry),
- Solid material which entered into the secondary system via a condenser leak,
- Resin beads from demineralizer, condensate polisher, or blowdown regenerative cleanup system leakage, and
- Foreign objects which were either left in the SGs directly or which were left in another portion of the secondary circuit and subsequently transported to the SGs.

Analysis of these materials can provide insight into the behavior of other components in the system, as well as information on the success or failure of foreign material exclusion (FME) programs. As illustrated in Figure C-6, most of these materials (along with spalled tube scale flakes) settle to the tubesheet. Therefore, in addition to hard and soft sludge, these materials are generally collected in deposit samples obtained during sludge lancing.

C.3 Variability in SG Deposit Properties

As may be expected based on the numerous different types of deposits, there is substantial variability in the SG deposits collected from different plants, during different outages at the same plant, and within a single SG during a single outage. Typical variabilities are discussed in the sub-sections below.

C.3.1 Variability within a SG

In addition to the variations between deposit types that were discussed above, individual types of deposits also vary within a SG. Combinations of the multiple types of tube scale depicted in Figure C-4 are often found within a single SG as a result both of variations in the operating history at the plant and differences in local thermal-hydraulic conditions throughout the bundle. For instance, regions of the tube bundle with the highest void fraction (i.e., highest steam quality) tend to have the thickest tube scale, which is believed to be as a result of increased boiling deposition. That said, in general tube scale properties (thickness, porosity, composition, etc.) tend to be relatively uniform when compared to variations in the properties of other deposit types (e.g., TTS collars).

In contrast, TTS collars tend to be very heterogeneous and properties may vary significantly even for TTS collars collected from the same SG during the same refueling outage (e.g., variations by a factor of 2-3 in aluminum concentration are not uncommon) [6]. The higher variability in properties for TTS collars, as compared to tube scale, is likely due to differences in the primary deposition mechanisms for these deposit types (e.g., gravitational settling and consolidation for TTS collars, as compared to boiling deposition for tube scale).

It is worth noting that additional variability in deposit properties within a SG may be introduced as a result of chemical or mechanical cleanings. This is particularly true if all deposits are not exposed to the same cleaning conditions, which may occur intentionally (e.g., during partial height chemical cleanings) or unintentionally (e.g., if a deep TTS sludge pile prevents the chemicals from accessing some of the deposits).

C.3.2 Outage-to-Outage Variability

Variability in deposit properties from outage to outage occur both as a result of actual changes, as well as apparent changes attributed to sampling differences. Because deposit properties tend change relatively slowly with time, sampling differences may be the primary cause of variations in deposit properties from outage-to-outage, and sampling differences should be considered when evaluating the significance of differences in deposit samples obtained at successive outages. In general, evaluating deposit properties over longer time periods tends to dampen the effects of sampling differences, and establish more meaningful statistical trends in actual deposit properties.

The properties of tube scale change over time, both as a result of the continued buildup of deposits and due to changes in plant operations (including both startup/shutdown evolutions and changes in nominal operating conditions). In the absence of any changes in plant operations, continued transport of deposit precursors to the SGs is expected to result in increasing scale thickness and decreasing scale porosity. Therefore, scale samples from later outages are generally expected to be thicker and less porous (although average tube scale thickness and porosity may change relatively slowly over time, as noted above). Tube scale composition tends to be relatively constant from outage-to-outage, except during the first few cycles and when significant plant changes occur (e.g., changes in chemistry control, major plant equipment, etc.)

The properties of TTS collars also evolve with time. However, since there is already significant variability in collar properties from piece to piece, changes in collar properties from outage-to-outage are typically similar to in magnitude to variability observed within a SG during a single outage [6]. Thus, it is generally challenging to establish trends in TTS collar properties with time. As noted above, it is generally thought that TTS collars continually grow by gravitational settling and consolidation of material present at the tubesheet. Thus, TTS collar composition is expected to evolve over time as a result of a number of random processes. TTS collars tend to grow in size consistently with time, but have little or no porosity regardless of collar age.

It is also worth noting that deposit management activities may result in relatively dramatic changes in deposit properties from outage to outage. For example, soft chemical cleaning processes may significantly increase the porosity of SG tube scale, and conventional ("hard") SG chemical cleaning processes may result in essentially complete removal of SG deposits. Thus, such maintenance activities should be considered when evaluating trends in deposit properties.

C.3.3 Plant-to-Plant Variability

The deposit properties at a particular plant will depend upon a number of factors, including:

- Plant materials of construction,
- Chemistry control,
- Years of operation,
- Deposit management history,
- Cooling water source,
- Condenser leakage, and
- SG design.

To the extent that these parameters vary between plants, the deposit properties are expected to vary as well.

In the case of tube scale, there is typically sufficient uniformity in the properties at a single plant that it is possible to make meaningful comparisons of the properties between plants. Typical ranges for key tube scale properties are as follows:

- Thickness: 2 to 10 mils (50 to 250 microns)
- Porosity: 5-30%
- Copper content: <0.1% to 50%

Due to the heterogeneity of TTS collars, it is difficult to distinguish plant-to-plant differences from general variations from piece to piece. Copper concentration in TTS collars typically vary from 1-50%, and as expected, higher copper concentrations are generally observed at plants with copper bearing alloys in BOP systems. Lead concentrations in TTS collars typically vary from 100 to 1000 ppm. As noted above, TTS collars have little or no porosity, and this observation is consistent from plant to plant. The size and thickness of TTS collar pieces vary significantly depending on chemistry control practices, the age of the SG and the manner in which the TTS collar piece was removed (among other factors).

D
EFFECTS OF STEAM GENERATOR DEPOSITS

The presence of deposits in SGs can lead to numerous operational issues, including corrosion of SG components (discussed in Section D.1), blockage of TSP flow passages (discussed in Section D.2), and degradation of heat transfer properties (discussed in Section D.3).

D.1 Corrosion of SG Tubing and Internals

Corrosion of SG components has historically been a significant issue affecting steam generator operations. In many cases, severe corrosion of Alloy 600MA tubing in original SGs forced utilities to replace the SGs after less than 15 EFPY. While replacement SGs utilize advanced materials such as Alloy 690TT and Alloy 800NG with improved corrosion resistance, laboratory tests and some field experience has shown that even these materials are not completely immune to all corrosion phenomena.

Boiling concentration of impurities can occur both in tube scale and in the TTS sludge pile, potentially leading to aggressive environments and the corrosion of the tubes, the tubesheet, and/or the tube supports. Additionally, the insulating effects of deposits (discussed in Section D.3) lead to higher temperatures at the surface of the tubes and, therefore, higher rates of corrosion (as many corrosion mechanisms are thermally activated). Finally, some corrosion products (e.g. copper oxides) can raise the electrochemical potential and thereby accelerate corrosion by mechanisms such as pitting and SCC. Therefore, continued SG maintenance is warranted in order to limit the risk of corrosion.

Several different types of corrosion effects are briefly reviewed in the subsections below. Additional discussion of corrosion phenomena can be found in the EPRI PWR Secondary Water Chemistry Guidelines [20].

D.1.1 OD IGA/SCC

The potential for outer diameter (OD) intergranular attack (IGA) and/or stress corrosion cracking (SCC) of SG tubes is significantly increased by the presence of deposits, particularly in TTS and TSP crevice regions. Some plants have also reported occurrences of OD IGA/SCC under heavy bridge-like (see Figure C-6) free span deposits. OD IGA/SCC is accelerated in both highly acidic (low pH) and highly caustic (high pH) conditions. ODSCC is more likely under oxidizing conditions, while IGA tends to occur under slightly reducing to slightly oxidizing conditions. Therefore, SG deposits tend to increase the likelihood of OD IGA/SCC both due to boiling concentration of impurities (for initial impurity ratios that concentrate to highly acidic or caustic solutions) and, in the case of SCC, when oxidized deposits such as copper oxides are present. Other impurities found in deposits, such as reduced sulfur species and lead, can also increase the risk of OD IGA/SCC.

As discussed in References [20] and [57], Alloys 690TT and 800NG have both been shown through lab testing and field service experience to be significantly more resistant than Alloy 600MA to corrosion mechanisms such as OD IGA/SCC. OD IGA/SCC has occurred in some operating SGs with Alloy 800NG tubing, while no cracking of Alloy 690TT has occurred. Alloy 600TT is also expected to be more resistant to corrosion than Alloy 600MA, although to a lesser extent than Alloy 690TT.

D.1.2 Denting

Denting is the deformation of tubes caused by the expansive corrosion of other SG components. Denting typically occurs due to the corrosion of constrained metallic components located adjacent to SG tubing. Denting has typically been most common in areas of the SG with significant deposit accumulation, such as the TTS. Deformation of the tubes by denting leads to increased stress levels and, therefore increases the risk of SCC. In severe cases, denting may result in diameter reductions that are significant enough to prevent the passage of inspection probes, thereby forcing utilities to plug affected tubes, even if no cracking has occurred.

Historically, the main cause of denting was the corrosion of carbon steel drilled hole TSPs (as well as other carbon steel tube supports, such as lattice bars and U-bend supports). Because of this, nearly all replacement generators have specified that TSPs be constructed from stainless steel (to improve corrosion resistance). More recently, denting has been observed in the top-of-the-tubesheet (TTS) region. Tubesheets are generally made from low-alloy steel (e.g., SA-508, Grade 3 Class 1). However, the minor amounts of alloying elements present in low-alloy steel are generally not expected to significantly improve the corrosion resistance of low alloy steels relative to carbon steel. Thus, in the same way that carbon steel corrosion in TSP crevices has led to denting at TSPs, corrosion of the tubesheet under deposits has led to denting at the TTS (including in replacement SGs with corrosion resistant materials). SCC associated with denting has occurred in SGs with Alloy 800NG tubes. Denting has also been observed in SGs with Alloy 690TT tubes, but no cracking has been observed in these SGs. Additional discussion on denting is available in Reference [15].

There is a significant correlation between the locations of the TTS sludge pile and the TTS dents at plants with recent occurrences of denting. As most denting is due to corrosion of carbon steel components, the mechanisms through which deposits affect denting are thought to mainly be the enhanced boiling concentration of impurities in the crevice and thermal insulation of the crevice leading to a more aggressive environment and overall higher rates of corrosion. The presence of oxidizing corrosion products (e.g., copper oxides) is not expected to directly play a significant role in causing denting, as the amount of tubesheet material required to be oxidized in order to cause denting is thought to be significantly more than the amount of oxidizing corrosion products transported to or formed in the tubesheet region. However, as discussed in Section D.1.1, oxidized corrosion products may be relevant to the occurrences of ODSCC associated with denting.

In addition to simply causing increased crevice temperatures and therefore increased corrosion rates, deposits are also thought to play a significant role in denting due to the thermohydraulic phenomenon of steam blanketing. Steam blanketing occurs when the available superheat (the difference between the local primary side temperature and the saturation temperature of bulk secondary side fluid) is high enough to prevent the ingress of liquid water into the crevice. This

protects the crevice from corrosion caused by highly concentrated secondary side impurities, and is thought to be one of the reasons why cold leg TTS dents have been more common than hot leg dents. In the presence of a TTS sludge pile, the available superheat on the hot leg is generally expected to be high enough that most crevices would be fully steam blanketed, while on the cold leg the available superheat is generally expected to be sufficient to cause some boiling concentration of impurities but not sufficient to cause full steam blanketing of the crevices.

As noted above, in some cases denting can be caused directly by the corrosion of metallic particles which have been transported to the SG and become incorporated into the TTS sludge pile. However, while TTS denting due to the corrosion of the tubesheet is expected to be an ongoing problem (until measures are implemented to reduce tubesheet corrosion), denting due to corrosion of metallic particles trapped in the sludge pile is generally expected to stop becoming worse once the metallic particles are fully corroded.

D.1.3 Pitting

Similar to OD IGA/SCC, the likelihood of pitting is increased due to acid oxidizing conditions and the presence of concentrated chlorides and partially reduced sulfur species. Therefore, the enhanced boiling concentration of impurities and the possibility of oxidizing species (e.g., copper oxides) due to the presence of deposits both increase the probability of pitting.

D.1.4 Wastage (Thinning)

Uniform general corrosion of tubing material is known as wastage or thinning. Wastage occurs under highly oxidizing and acidic conditions, and was a significant issue at many plants which were operating (or had previously operated) on phosphate water chemistry (although it can also occur in highly concentrated sulfate solutions). Deposits accelerate wastage due to boiling concentration of aggressive species and increased tube surface temperatures.

D.2 Blockage of TSP Flow Passages

In addition to the TTS and tubing freespan, deposits can form in TSP flow passages and cause numerous operational issues such as level instability, flow-induced vibration and flow accelerated corrosion. These issues are discussed in the sub-sections below.

D.2.1 Level Instability / Oscillations

One significant effect of TSP blockages is an increased pressure drop through the tube bundle, which leads to a lower overall flowrate through the tube bundle. Given a constant thermal output from the core, a lower flowrate necessarily causes an increase in the steam quality (vapor fraction of the water) leaving the bundle. Higher vapor fractions are associated with a decreased ability to dampen flow and level oscillations. These issues become more severe with increased TSP blockages. The only short term remedial measure available to prevent such oscillations is to reduce the plant's power output in order to decrease the vapor fraction of the water leaving the SG. Such power reductions are costly, and mechanical and/or chemical cleaning techniques are typically applied as soon as practical in order to remove the blockages and allow full power operation to be resumed. Historically, this issue has been more common in once-through steam generators (OTSGs), but it has also occurred in recirculating steam generators (RSGs).

D.2.2 Flow-Induced Vibration and Fretting / Wear

Another effect of TSP blockages is to disrupt the normal flow patterns through the SGs. This disruption can lead to tube vibration-related failures as have been observed at several EDF units [2, 3]. Deposits at TSPs can also lock the tubes in place, which increases the mean stress in the tubing and increases the rate of fatigue crack propagation.

S.2.3 Flow Accelerated Corrosion

Another potential effect of changes in flow patterns due to deposit buildup is an increase in flow accelerated corrosion (FAC) of carbon steel components. This was previously a significant issue in SGs with carbon steel eggcrate TSPs. However, since stainless steel TSPs are typically used in replacement SGs, FAC of TSPs due to TSP blockage is no longer considered to be a significant concern.

D.3 SG Tube Fouling

Deposit accumulations can also lead to SG tube fouling and heat transfer efficiency loss, which can result in decreased secondary side pressure and plant power. Tube scale is the primary deposit type that impacts heat transfer efficiency. Initially, tube scale can lead to improved heat transfer characteristics relative to clean heat exchanger tubes. This occurs due to the formation of a porous wick and chimney structure as described above. However, as plant operation continues, the porosity of tube scale gradually decreases, as does the heat transfer efficiency. This is thought to occur as wicks (and eventually the larger chimneys) gradually fill with salts, retrograde solubility species, aluminosilicates, copper metal, and/or iron oxide. Case studies on steam generator thermal performance degradation are described in prior reports such as EPRI TR-110018 [37].

Soft chemical cleaning is the primary technique that has been used by utilities to address SG heat transfer losses. Soft cleanings have been very effective at reestablishing porous tube scale structures that are beneficial with respect to heat transfer efficiency, resulting in significant heat transfer benefits [7]. Soft cleaning processes have also been effective for reducing TSP blockages and eliminating associated consequences such as level oscillations.

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Electric Power Research Institute
3420 Hillview Avenue, Palo Alto, California 94304-1338 • PO Box 10412, Palo Alto, California 94303-0813 USA
800.313.3774 • 650.855.2121 • askepri@epri.com • www.epri.com