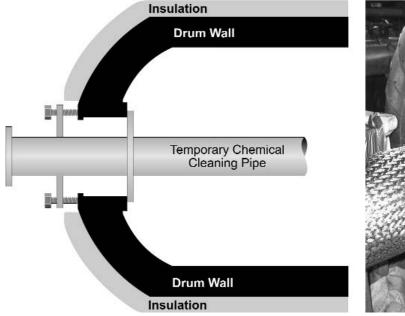


Heat Recovery Steam Generator (HRSG) Chemical Cleaning Guidelines Case Studies



Technical Report





Heat Recovery Steam Generator (HRSG) Chemical Cleaning Case Studies

1012756

Final Report, November 2006

EPRI Project Manager K. Shields

DISCLAIMER OF WARRANTIES AND LIMITATION OF LIABILITIES

THIS DOCUMENT WAS PREPARED BY THE ORGANIZATION(S) NAMED BELOW AS AN ACCOUNT OF WORK SPONSORED OR COSPONSORED BY THE ELECTRIC POWER RESEARCH INSTITUTE, INC. (EPRI). NEITHER EPRI, ANY MEMBER OF EPRI, ANY COSPONSOR, THE ORGANIZATION(S) BELOW, NOR ANY PERSON ACTING ON BEHALF OF ANY OF THEM:

(A) MAKES ANY WARRANTY OR REPRESENTATION WHATSOEVER, EXPRESS OR IMPLIED, (I) WITH RESPECT TO THE USE OF ANY INFORMATION, APPARATUS, METHOD, PROCESS, OR SIMILAR ITEM DISCLOSED IN THIS DOCUMENT, INCLUDING MERCHANTABILITY AND FITNESS FOR A PARTICULAR PURPOSE, OR (II) THAT SUCH USE DOES NOT INFRINGE ON OR INTERFERE WITH PRIVATELY OWNED RIGHTS, INCLUDING ANY PARTY'S INTELLECTUAL PROPERTY, OR (III) THAT THIS DOCUMENT IS SUITABLE TO ANY PARTICULAR USER'S CIRCUMSTANCE; OR

(B) ASSUMES RESPONSIBILITY FOR ANY DAMAGES OR OTHER LIABILITY WHATSOEVER (INCLUDING ANY CONSEQUENTIAL DAMAGES, EVEN IF EPRI OR ANY EPRI REPRESENTATIVE HAS BEEN ADVISED OF THE POSSIBILITY OF SUCH DAMAGES) RESULTING FROM YOUR SELECTION OR USE OF THIS DOCUMENT OR ANY INFORMATION, APPARATUS, METHOD, PROCESS, OR SIMILAR ITEM DISCLOSED IN THIS DOCUMENT.

ORGANIZATION(S) THAT PREPARED THIS DOCUMENT

Sheppard T. Powell Associates, LLC

NOTICE: THIS REPORT CONTAINS PROPRIETARY INFORMATION THAT IS THE INTELLECTUAL PROPERTY OF EPRI. ACCORDINGLY, IT IS AVAILABLE ONLY UNDER LICENSE FROM EPRI AND MAY NOT BE REPRODUCED OR DISCLOSED, WHOLLY OR IN PART, BY ANY LICENSEE TO ANY OTHER PERSON OR ORGANIZATION.

NOTE

For further information about EPRI, call the EPRI Customer Assistance Center at 800.313.3774 or e-mail askepri@epri.com.

Electric Power Research Institute and EPRI are registered service marks of the Electric Power Research Institute, Inc.

Copyright © 2006 Electric Power Research Institute, Inc. All rights reserved.

CITATIONS

This report was prepared by

Sheppard T. Powell Associates, LLC 1915 Aliceanna Street Baltimore, MD 21231

Principal Investigators R. Bartholomew G. Roberts

Report Contributors

Sheppard T. Powell Associates, LLC E. Hull

Dennis A. Frey Consultants D. Frey

George Bodman, Inc. G. Bodman M. Bayse

This report describes research sponsored by the Electric Power Research Institute (EPRI).

The report is a corporate document that should be cited in the literature in the following manner:

Heat Recovery Steam Generator (HRSG) Chemical Cleaning Case Studies. EPRI, Palo Alto, CA: 2006. 1012756.

PRODUCT DESCRIPTION

A considerable number of combined cycle units with heat recovery steam generators (HRSGs) were installed over the past two decades worldwide, and the design complexity and operating pressures of these units increased significantly during this period. One of the goals of EPRI's Heat Recovery Steam Generator (HRSG) Dependability Program 88 is to minimize availability losses associated with HRSG tube failures. To support its members operating combined cycle units, EPRI published *Heat Recovery Steam Generator (HRSG) Chemical Cleaning Guidelines* in 2003 (EPRI report 1004499). Due to limited operational cleaning experiences in HRSGs, these comprehensive guidelines for chemical cleaning were based primarily on a combination of available preoperational cleaning experience for HRSG units and proven operational cleaning experience of conventional boilers. Unfortunately, for those HRSG units with significant accumulations of operational deposits, operational cleanings case studies that discuss operationally formed deposits, cleaning system designs, and the solvents and procedures used to clean HRSG units.

Results & Findings

The case study presentations discuss at length a variety of deficiencies in planning and performance from known operational cleaning experiences across the industry. The report evaluates the reasons for deficient cleaning efforts and identifies and discusses needed improvements based on available experience. For the most part, the HRSG cleaning operations described in these cases were not conducted according to available EPRI guidelines for either cycle chemistry in combined cycle units with HRSGs or for chemical cleaning of HRSGs.

Challenges & Objectives

HRSG tube failures and chemical cleanings can incur substantial expenditures of time and money. Evaluating HRSG cleanliness and developing and performing effective cleanings require expert guidance. These case studies demonstrate the challenges faced by individuals conducting these activities and the results obtained at other HRSG facilities.

Failure to clean or the performance of an improper chemical cleaning may contribute to subsequent chemistry control problems and potential evaporator tube damage. For example, one of the case studies indicated that an improperly performed chemical cleaning resulted in deposit formation during the chemical cleaning and subsequent phosphate hideout following return of the unit to service.

Applications, Values & Use

The case study accounts provided in this report may be used as a supplement to the 2003 guidelines when assessing HRSG unit cleanliness or planning and performing a chemical cleaning. The case studies also suggest some alternative approaches to chemical cleaning that are

not delineated in the 2003 chemical cleaning guidelines. Due to the costs associated with chemical cleaning, some organizations have elected to use nonchemical methods for controlling deposits in HRSG units. In order to defer or avoid chemical cleaning of HRSG units, hydrojetting of evaporator tubes was performed for a number of HRSG units, where allowed by HRSG designs or other circumstances.

EPRI Perspective

This case study assessment identifies a number of possible problems that have been experienced during known operational chemical cleanings at HRSG facilities. It also describes lessons learned from these efforts and describes useful approaches for effective planning and performance of operational cleanings of HRSG units. The case studies provide many examples of the possible consequences of not assessing waterside cleanliness and cleaning requirements as indicated in the 2003 guidelines. Users of the guidelines can avoid many of these problems and by implementing the improved approaches discussed in these case studies are more likely to obtain satisfactory results. In some instances, further work to improve the understanding of HRSG cleaning requirements should be considered.

Approach

Using the internal records of several consulting firms, the project team compiled a knowledge base on known operational cleanings of HRSGs including information on the reasons chemical cleaning was undertaken, the characteristics of deposits, cleaning procedures, field experience, and results. Requests to other organizations in the industry yielded additional information on tube failures and operational cleanings. In some instances the input available was incomplete yet useful in defining the existing base of operational cleaning experience. The team developed a number of case studies to illustrate the key lessons learned from the available information.

Keywords

Heat recovery steam generator (HRSG) Combined cycle units Evaporator tube deposits Deposit weight Chemical cleaning Deposit removal Hydrojetting

ABSTRACT

During the past two decades, a relatively small number of operating HRSG units are known to have experienced tube failures related to waterside deposits. Response to these failures has included tube replacement, chemical cleaning, and hydrojetting.

Owners of some HRSG units have elected to perform operational chemical cleanings in an effort to clean waterside surfaces following chemistry upsets or as a result of videoscopic inspections. Only a few facilities are known to have performed chemical cleanings on a relatively fixed period of operation. Tremendous deposit accumulations have been found in some HRSG units, and better monitoring methods are needed for use at HRSG facilities to track deposit accumulations in evaporators.

In 2003, EPRI published *Heat Recovery Steam Generator (HRSG) Chemical Cleaning Guidelines* to assist personnel at HRSG facilities with the tasks of evaluating waterside deposits and developing appropriate chemical cleaning procedures for preoperational and operational cleanings. However, this document largely considered available HRSG preoperational cleaning experience and operational cleaning approaches developed for conventional boilers. It was expected that the Guidelines would need to be revised once broader experience had been acquired on deposition activity and operational cleanings of HRSG units.

The report reviews several operational cleanings case studies that discuss operationally formed deposits, cleaning system designs, and the solvents and procedures used to clean HRSG units. The greatest single problem with performing an effective chemical cleaning of HRSG units appears to have been establishing adequate distribution and circulation of solvents and passivation solutions. Organic solvents generally require fairly uniform circulation. To determine if reasonably good circulation is possible, a hydraulic evaluation should be performed on the HRSG before selecting a solvent or developing a bid specification for the cleaning. In some cases, combinations of blend filling, moderate circulation, and long contact times can enable the use of organic solvents and passivation solutions. However, in other cases, strong mineral acids have been used to operationally clean HRSG units. The latter may deserve greater consideration by HRSG facilities for future chemical cleanings.

In addition to the chemical cleaning of HRSG units, hydrojetting of evaporator tubes was performed for a number of HRSG units. Use of hydrojetting or other mechanical methods for deposit removal may require greater consideration in future guidelines.

ACKNOWLEDGMENTS

The authors would like to express their sincerest gratitude to all individuals who contributed data for this project and reviewed draft versions of this document. In addition to the individuals listed under Citations, helpful information was provided by Mr. Richard Breckenridge of Arizona Public Service Company and Mr. William Stroman of Primary Energy. All graphics for this report were produced by Mr. Daniel G. Whittemore of Sheppard T. Powell Associates, LLC. Word processing of text and tables was performed by Mrs. Sara T. Colbert-Woodland of Sheppard T. Powell Associates, LLC.

CONTENTS

1	INTRODUCTION	1-1
	1.1 Introduction	1-1
	1.2 Objectives	1-2
	1.3 Reasons for Cleaning	1-3
	1.4 Methods Used to Evaluate Cleanliness	1-4
	1.5 Cleaning System Design and Planning	1-4
	1.6 Cleaning Solvents and Procedures Used	1-5
	1.7 Results and Lessons Learned	1-6
	1.8 Reference	1-7
2	CHEMICAL CLEANING CASE STUDIES	2-1
	2.1 Overview	2-1
	2.2 Case Study 1: Chelant Cleanings of Triple-Pressure, Drum-Type HRSG Ur	nits2-2
	2.2.1 Unit Design	2-2
	2.2.2 Operational History and Reason for Cleaning	2-2
	2.2.3 Evaluating Deposits and Cleaning Requirements	2-3
	2.2.4 Cleaning System Design	2-3
	2.2.4.1 HP Evaporator Cleaning System	2-3
	2.2.4.2 IP and LP Evaporator Cleanings	2-8
	2.2.5 Cleaning Procedure and Results	2-8
	2.2.6 Lessons Learned	2-11
	2.3 Case Study 2: Chelant Cleaning of Dual-Pressure, Drum-Type HRSG Unit	2-13
	2.3.1 Unit Design	2-13
	2.3.2 Operational History and Reason for Cleaning	2-13
	2.3.3 Evaluating Deposits and Cleaning Requirements	2-14
	2.3.4 Cleaning System Design	2-14
	2.3.5 Cleaning Procedure and Results	2-15

2.3.6 Lessons Learned	2-18
2.4 Case Study 3: Cleaning of a Dual-Pressure Drum-Type Evaporator with a Citric/Phosphoric Acid Mixture	2 10
2.4.1 Unit Design	
2.4.2 Operational History and Reason for Cleaning	
2.4.3 Evaluating Deposits and Cleaning Requirements	
2.4.4 Cleaning System Design	
2.4.5 Cleaning Procedure and Results	
2.4.5.1 Postcleaning Deposit Evaluation	
2.4.6 Lessons Learned	
2.5 Case Study 4: Planning for Cleaning of a Once-Through HRSG Unit	
2.5.1 Unit Design	
2.5.2 Operational History and Reason for Cleaning	
2.5.3 Evaluating Deposits and Cleaning Requirements	
2.5.4 Cleaning System Design	
2.5.5 Chemical Cleaning Procedure and Results	
2.5.6 Lessons Learned	2-28
2.6 Case Study 5: Hydrochloric Acid Cleaning of Single Pressure HRSG	2-28
2.6.1 HRSG Design	2-28
2.6.2 Operational History and Reason for Cleaning	2-28
2.6.3 Evaluating Cleaning Requirements and Deposits	2-29
2.6.4 Cleaning System Design	2-29
2.6.5 Cleaning Procedure and Results	2-31
2.6.5.1 Preheat Stage	2-31
2.6.5.2 Iron Oxide Removal	2-31
2.6.5.3 Passivation Stage	2-32
2.6.5.4 Postcleaning Activities and Recommendations	2-32
2.6.6 Lessons Learned	2-32
2.7 Case Study 6: Hydrochloric Acid Cleaning of Evaporator Followed by	
Ammoniated Citric Acid Cleaning of Superheater and Evaporator	
2.7.1 HRSG Design	
2.7.2 Operational History and Reason for Cleaning	
2.7.3 Evaluating Deposits and Cleaning Requirements	2-33
2.7.4 Cleaning System Design	2-34

2.7.5 Chemical Cleaning Procedure and Results	2-34
2.7.6 Lessons Learned	2-39
2.8 Case Study 7: Dual-Pressure HRSG, Acid Phosphate Corrosion, Sodium	
Cleaning	
2.8.1 HRSG Design	
2.8.2 Operational History and Reason for Cleaning	
2.8.3 Evaluating Deposits and Cleaning Requirements	2-40
2.8.4 Chemical Cleaning Procedure and Results	2-41
2.8.5 Lessons Learned	2-42
2.9 Case Study 8: Dual-Pressure HRSG, Chelant Cleaning	2-42
2.9.1 HRSG Design	2-42
2.9.2 Operational History and Deposit Evaluation	2-42
2.9.3 Chemical Cleaning Design	2-42
2.9.4 Cleaning Procedure and Results	2-43
2.9.4.1 Passivation	2-43
2.9.5 Lessons Learned	2-43
2.10 Other Case Studies	2-44
2.11 References	2-44
3 ALTERNATIVES TO CHEMICAL CLEANING	3-1
<i>3</i> ALTERNATIVES TO CHEMICAL CLEANING 3.1 Introduction	3-1 3-1
 <i>3</i> ALTERNATIVES TO CHEMICAL CLEANING. 3.1 Introduction	3-1 3-1 3-2
 <i>3</i> ALTERNATIVES TO CHEMICAL CLEANING. 3.1 Introduction 3.2 Case Study 13: Tube Replacement	3-1 3-1 3-2 3-4
 3 ALTERNATIVES TO CHEMICAL CLEANING. 3.1 Introduction 3.2 Case Study 13: Tube Replacement 3.3 Case Study 14: Hydrojetting Single Pressure, Two-Drum HRSG 3.3.1 HRSG Design 	3-1 3-1 3-2 3-4 3-4
 3 ALTERNATIVES TO CHEMICAL CLEANING. 3.1 Introduction 3.2 Case Study 13: Tube Replacement 3.3 Case Study 14: Hydrojetting Single Pressure, Two-Drum HRSG 3.3.1 HRSG Design 3.3.2 Operating History and Deposit Evaluation 	3-1 3-1 3-2 3-4 3-4 3-4 3-4
 3 ALTERNATIVES TO CHEMICAL CLEANING. 3.1 Introduction 3.2 Case Study 13: Tube Replacement 3.3 Case Study 14: Hydrojetting Single Pressure, Two-Drum HRSG 3.3.1 HRSG Design 	3-1 3-1 3-2 3-4 3-4 3-4 3-4
 3 ALTERNATIVES TO CHEMICAL CLEANING. 3.1 Introduction 3.2 Case Study 13: Tube Replacement 3.3 Case Study 14: Hydrojetting Single Pressure, Two-Drum HRSG 3.3.1 HRSG Design 3.3.2 Operating History and Deposit Evaluation 	3-1 3-1 3-2 3-4 3-4 3-4 3-4 3-5
 3 ALTERNATIVES TO CHEMICAL CLEANING. 3.1 Introduction 3.2 Case Study 13: Tube Replacement 3.3 Case Study 14: Hydrojetting Single Pressure, Two-Drum HRSG 3.3.1 HRSG Design 3.3.2 Operating History and Deposit Evaluation 3.3.3 Mechanical Deposit Removal by Hydrojetting 	3-1 3-1 3-2 3-4 3-4 3-4 3-4 3-5 3-5
 3 ALTERNATIVES TO CHEMICAL CLEANING. 3.1 Introduction 3.2 Case Study 13: Tube Replacement 3.3 Case Study 14: Hydrojetting Single Pressure, Two-Drum HRSG 3.3.1 HRSG Design 3.3.2 Operating History and Deposit Evaluation 3.3 Mechanical Deposit Removal by Hydrojetting 3.4 Case Study 15: Hydrojetting Single Pressure, Two-Drum HRSG 	3-1 3-1 3-2 3-4 3-4 3-4 3-4 3-5 3-5 3-5
 3 ALTERNATIVES TO CHEMICAL CLEANING. 3.1 Introduction 3.2 Case Study 13: Tube Replacement	3-1 3-1 3-2 3-4 3-4 3-4 3-5 3-5 3-5 3-5 3-5
 3 ALTERNATIVES TO CHEMICAL CLEANING. 3.1 Introduction	
 3 ALTERNATIVES TO CHEMICAL CLEANING. 3.1 Introduction 3.2 Case Study 13: Tube Replacement 3.3 Case Study 14: Hydrojetting Single Pressure, Two-Drum HRSG 3.3.1 HRSG Design 3.3.2 Operating History and Deposit Evaluation. 3.3.3 Mechanical Deposit Removal by Hydrojetting 3.4 Case Study 15: Hydrojetting Single Pressure, Two-Drum HRSG 3.4.1 HRSG Design 3.4.2 Operating History and Deposit Evaluation. 3.4.2 Operating History and Deposit Evaluation. 3.4.3 Mechanical Deposit Removal by Hydrojetting . 	3-1 3-1 3-2 3-4 3-4 3-4 3-5 3-5 3-5 3-5 3-5 3-5 3-7 3-7 3-7
 3ALTERNATIVES TO CHEMICAL CLEANING. 3.1 Introduction 3.2 Case Study 13: Tube Replacement 3.3 Case Study 14: Hydrojetting Single Pressure, Two-Drum HRSG 3.3.1 HRSG Design 3.3.2 Operating History and Deposit Evaluation 3.3 Mechanical Deposit Removal by Hydrojetting 3.4 Case Study 15: Hydrojetting Single Pressure, Two-Drum HRSG 3.4.1 HRSG Design 3.4.2 Operating History and Deposit Evaluation 3.4.3 Mechanical Deposit Removal by Hydrojetting 3.5 Case Study 16: Hydrojetting in Lieu of Chemical Cleaning 3.6 References 	
 3 ALTERNATIVES TO CHEMICAL CLEANING. 3.1 Introduction 3.2 Case Study 13: Tube Replacement 3.3 Case Study 14: Hydrojetting Single Pressure, Two-Drum HRSG 3.3.1 HRSG Design 3.3.2 Operating History and Deposit Evaluation 3.3 Mechanical Deposit Removal by Hydrojetting 3.4 Case Study 15: Hydrojetting Single Pressure, Two-Drum HRSG 3.4.1 HRSG Design 3.4.2 Operating History and Deposit Evaluation 3.4.3 Mechanical Deposit Removal by Hydrojetting 3.4.3 Mechanical Deposit Removal by Hydrojetting 3.5 Case Study 16: Hydrojetting in Lieu of Chemical Cleaning 	3-1 3-1 3-2 3-4 3-4 3-4 3-4 3-5 3-5 3-5 3-5 3-5 3-7 3-7 3-7 3-9 3-9

4.2 Reasons for Cleaning	4-1
4.3 HRSG Deposit Evaluations	4-1
4.4 Planning for Chemical Cleaning	4-2
4.4.1 Solvent Distribution and Circulation	4-2
4.4.2 Solvent Selection	4-3
4.4.3 Miscellaneous Planning Considerations	4-3
4.5 Chemical Cleaning Solvents and Procedures	4-4
4.6 Chemical Cleaning Deferment	4-5
4.7 Conclusion and Future Needs	4-5
4.8 References	4-7

LIST OF FIGURES

Figure 2-1 Case Study 1: HP Evaporator-Economizer Cleaning	2-4
Figure 2-2 Case Study 1: Steam Drum Manway Connection for Temporary Chemical Cleaning Piping	2-7
Figure 2-3 Case Study 1: IP Evaporator/Economizer/Superheater Cleaning	2-9
Figure 2-4 Case Study 1: LP Evaporator/Preheater/Superheater Cleaning	2-10
Figure 2-5 Case Study 2: Cleaning System Design	2-16
Figure 2-6 Case Study 2: Iron Oxide Removal	2-17
Figure 2-7 Case Study 2: Total EDTA and System Volume Estimates During Iron Oxide Removal Stage	
Figure 2-8 Case Study 2: Solvent pH During Iron Oxide Removal	2-19
Figure 2-9 Case Study 3: Simplified Drawing of HRSG Cleaning System	2-22
Figure 2-10 Case Study 4: Simplified Cleaning System Schematic	2-27
Figure 2-11 Case Study 5: HRSG with a Sweet Water Condenser	2-30
Figure 2-12 Case Study 6, Hydrochloric Acid Stage Chemistry Data	2-36
Figure 2-13 Case Study 6: Ammoniated Citric Acid Cleaning Iron Concentration Data	2-37
Figure 3-1 Case Study 13 Tube Sample	3-3
Figure 3-2 Case Study 15, Typical Evaporator Tube Before Hydrojetting	3-7
Figure 3-3 Case Study 16: Evaporator Tube before Hydrojetting	3-9

LIST OF TABLES

Table 1-1 Summary of HRSG Operational Chemical Cleaning Case Studies
Table 2-1 Case Study 3, Simplified Summary of Hydraulic Evaluation 2-23

1 INTRODUCTION

1.1 Introduction

In 2003, EPRI produced the first comprehensive chemical cleaning guidelines specific to Heat Recovery Steam Generators (HRSGs). ⁽¹⁾ Of necessity, the 2003 guidelines drew heavily on both the experience gained from preoperational cleanings of HRSG units and from operational cleanings of conventional boilers. At the time the guidelines were produced, there was limited operational cleaning experience for HRSG units. It was anticipated that the guidelines would require updating when more experience had been obtained with operational deposits and cleaning requirements for these units. The primary aim of this project was to examine information currently available on cleanings performed to date and determine what lessons can be learned from these efforts so as to provide better guidance to organizations planning their own cleanings. It also will be useful in determining the adequacy and relevancy of the 2003 guidelines and in scheduling a time for their revision.

The project team consists of a group of consultants and was selected due to its broad collective experience in the area of chemical cleaning of steam generators and other industrial equipment. This approach was taken because the number of known operational cleanings of HRSGs is still quite small. Table 1-1 provides a summary of the cleaning experience considered by the project team in the development of this document.

The population of facilities summarized in Table 1-1 includes combined cycle plants as well as some plants with HRSGs designed for industrial cogeneration. In all, 16 facilities at which operational chemical cleanings of HRSGs were considered have been evaluated. In some instances, alternatives to chemical cleaning such as extensive tube replacement and mechanical removal of deposits by hydrojetting were implemented. From this case study population, eight chemical cleaning case study discussions (Case Studies 1-8 in Table 1-1) were developed and are presented in Section 2. Four additional cases studies (Case Studies 13-16 in Table 1-1), in which actions other than chemical cleaning were taken are presented in Section 3.

Introduction

Case Study (Report Section)	HP Evaporator Pressure, psi (MPA)	Evaporator Tube Failures	Deposit Loading ^(a) , g/ft ² (mg/cm ²)	Corrective Action Taken (Number of HRSGs)
1 (2.2)	1940 (13.4)	Yes	88 (~95)	Chemical Clean (2)
2 (2.3)	Unknown	No		Chemical Clean (1)
3 (2.4)	1400 (9.7)	No		Chemical Clean (2)
4 (2.5)	1500 (10.0)	No		Chemical Clean (1)
5 (2.6)	600 (4.1)	No		Chemical Clean (1)
6 (2.7)	425 (2.9)	Yes	41 (~44)	Chemical Clean (1)
7 (2.8)	1550 (10.7)	Yes	300 (~323)	Chemical Clean (2)
8 (2.9)	1020 (7.0)	Yes		Chemical Clean (4)
9 ()	700 (4.8)	Unknown	75.17 (~81) ^(b)	Chemical Clean (1)
10 ()	<1500 (<10.3)	Unknown		Chemical Clean (1)
11 ()	Unknown	Yes		Chemical Clean (1)
12 ()	2000 (13.8)	Yes	>700 (~753)	Chemical Clean (2)
13 (3.2)	2100 (14.5)	Yes	822.6 (~885)	Replace Tubes (1)
14 (3.3)	900 (6.2)	Yes	Heavy ^(c)	Hydrojetting (2)
15 (3.4)	700 (4.8)	Yes		Hydrojetting (16)
16 (3.5)	650 (4.5)	Yes	Heavy ^(c)	Hydrojetting (1)

Table 1-1
Summary of HRSG Operational Chemical Cleaning Case Studies

^(a) Mechanical method of deposit removal, ASTM D3483, Method-A.

^(b) This older facility had a program of periodic tube sampling.

^(c) Tubes in these units were either completely plugged or nearly completely plugged with deposit material.

1.2 Objectives

The project objectives were to characterize available HRSG operational experience with emphasis on the following aspects.

- Reasons for cleaning.
- Methods being used to evaluate HRSG deposits and cleaning requirements.
- Cleaning system design and planning.
- Cleaning solvents and procedures used.

• Results and lessons learned.

These findings are briefly summarized in the following sections.

1.3 Reasons for Cleaning

By far, HRSG tube failures are the main reason chemical cleaning has been performed. Information was obtained from 10 facilities which had experienced evaporator tube failures in their HRSG units. Not all failures occurred during service, and only 12 of the HRSG units with tube failures were chemically cleaned. Reasons indicated for the 19 operational chemical cleanings in the database compiled by the project team included the following. (Note that a facility may have elected to clean for more than one reason.)

- Evaporator tube failures during service in at least seven HRSGs. (There were other HRSG units with evaporator tube failures during service, but chemical cleaning was not always performed.)
- Visual or videoscopic indication of preoperational corrosion products and out-of-service freeze damage failures in four peaking HRSG units (caused by small diameter drains that were plugged with corrosion products).
- A pulp and paper company that has two HRSGs employs a point system by which they clean conventional boilers, and now their HRSG units, within a fixed period of time.
- Turbine deposition downstream of one HRSG of once-through design.
- Makeup water treatment system failure (100 hours past demineralizer exhaustion) was cited for two HRSGs.
- Essentially no chemistry control during operation was the reason for cleaning one HRSG.
- Massive condenser leaks necessitated cleaning of a single HRSG.
- Tube sampling results this HRSG was indicated to have been cleaned every two to three years. At the time of the cleaning evaluation on which the case study is based, the unit had been in operation for 24 years. However, it is likely that this unit experienced tube failures at some point in the past operation of the plant to justify the frequent cleaning interval.
- The underlying reason for the cleaning of one HRSG was not reported but chip scale deposits removed from the HRSG consisted primarily of hardness, phosphate and silica, indicating an intrusion of untreated water into the feedwater system.

Reasons dirty HRSGs in the database were not chemically cleaned include the following listed items. Some of the facilities indicated more than one reason for their decision.

- All tubes of one HRSG were replaced (tube damage was too extensive).
- After partial tube replacement in HRSG units at three case study facilities, it was demonstrated that other affected tubes could be cleaned by hydrojetting. Use of this option is most practical for HRSG units with a conventional generation bank arrangement with easily

Introduction

accessible upper and lower drums. However, hydrojetting has also effectively used to remove operational deposits from internal surfaces of HRSG evaporator tubes by cutting into the upper evaporator headers in HRSGs of less accessible design.

- Management elected to delay cleaning (and no additional failures were experienced) after a partial tube replacement in two HRSGs.
- Underdeposit corrosion, appearing as pitting damage, has not reached a level to cause failures in one HRSG.

The time the HRSG units were in service prior to cleaning or other corrective action varied considerably within the case study population. In over 60 per cent of the facilities corrective action was needed in the first three years of operation, including many events that necessitated action after less than one year of service. Of the remaining facilities only one of the facilities with a low pressure cycle design operated for more than 10 years before operational cleaning was considered.

1.4 Methods Used to Evaluate Cleanliness

For the facilities with HRSGs discussed herein, the methods used to evaluate HRSG cleanliness included the following.

- Visual inspections of drums.
- Videoscopic inspection of tubes and headers.
- Tube sampling.
- Review of steam/water cycle chemistry records.

The design of HRSGs is not conducive to tube sampling and in several of the case studies summarized in Table 1-1 corrective action was initiated without collection and analysis of any tube samples. In those instances where tube samples were taken, findings revealed high levels of deposition without any strong correlation to HRSG design, operating pressure or application.

As the new fleet of combined cycle plants with HRSGs accrues service hours unit operators need to be aware of the possibility of deposition activity and make provision to assess it. Improved techniques for appraising HRSG tube cleanliness above and beyond the methods used in conventional boilers are needed as such techniques would enable better and more frequent internal assessments. This approach make it easier to maintain evaporator tube cleanliness, which is needed to attain the highest level of combined cycle unit dependability.

1.5 Cleaning System Design and Planning

The most difficult aspects when designing an effective operational cleaning system are establishing adequate solvent distribution and circulation. Preoperational cleaning system circulation, temperature, and chemistry can be wholly inadequate for removal of deposits

following periods of operation. This has been found to be particularly true for procedures employing organic acids or chelants as the solvent.

Differences in the deposit removal performance of operational cleanings compared to preoperational cleanings are believed to be due partially to the much heavier deposits present following periods of operation. Also, changes may occur in deposit morphology or crystal structure when exposed to high tube metal temperatures. Preoperational deposits normally consist of minor amounts of two types of iron oxides - mill scale and sometimes a porous layer of rust. Mill scale is adherent but usually fairly thin. Porous rust formed under ambient temperatures can be partially hydrated and rather easily dissolved. These preoperational iron oxide layers usually are fairly easy to remove through chemical cleaning. However, deposits which remain on tube surfaces for long periods of operation appear to become both denser and more adherent. Operational deposits can contain mixtures of metal oxides and other materials such as hardness (calcium and magnesium), phosphate, silica, etc., which can be more difficult to remove. Concentration of the evaporator water beneath porous deposits. Also, tubes which have experienced high temperature conditions can have particularly hard and adherent waterside deposit accumulations.

Organic acid or chelant based solvents require circulation for adequate performance. However, with some HRSG designs, localized HP evaporator tube velocities can be orders of magnitude lower than the calculated average velocity for the HP evaporator. For drum type HRSG units, low solvent velocities can result from restrictions in the feeder pipes (some even have orifices installed) to the individual harps or groups of harps. For the preoperational cleanings, sometimes the deposits were so easy to remove that essentially no circulation was required. In other cases, extensive circulation systems were designed for preoperational cleanings.

Even in facilities where extensive circulation was provided for preoperational cleanings, further calculations on some of these systems have indicated that they may be inadequate for operational cleanings.

1.6 Cleaning Solvents and Procedures

The following inhibited solvents were used for operational chemical cleaning of HRSG units.

- Diammonium EDTA.
- Monoammonium Citrate with Ammonium Bifluoride.
- Sodium Citrate.
- Hydrochloric Acid with Thiourea and Ammonium Bifluoride.
- Proprietary Blends (A mixture of phosphoric and citric acids was one of the proprietary blends used, unsuccessfully, to clean a HRSG unit.)

Introduction

The use of hydrochloric acid was restricted to the cleaning of small, older style HRSG units. However, problems with achievement of satisfactory circulation of some HRSG units when cleaning with organic solvents may require greater consideration of hydrochloric acid (or possibly hydrofluoric acid) for operational cleanings. In one case, a hydrochloric acid cleaning of the evaporator was performed, the unit was rinsed, and then an organic solvent cleaning of the superheaters was performed to remove carryover deposits from the evaporators. One problem with a hydrochloric acid cleaning of evaporators is being able to ensure complete removal of any sludge that may contain acid. Acid-laden sludges must be completely removed in order to avoid subsequent corrosion during or after the passivation stage.

While the EPRI guidelines for chemical cleaning of HRSG units ⁽¹⁾ specify high temperatures for both preoperational and operational cleanings, most vendors and facilities have utilized much lower temperatures for preoperational cleanings. While it has been believed, generally, that the lower temperatures used during preoperational cleanings with EDTA and citrate cleaning solvents were satisfactory for mill scale and rust removal, tube sampling or postcleaning videoscopic inspection have not been performed following preoperational cleanings to confirm the effectiveness of the cleaning operation. Also, reduced cleaning temperatures have been found to be inadequate for operational cleanings. Therefore, it appears that the high temperatures advised in the HRSG cleaning guidelines for EDTA and citrate are appropriate also for operational cleanings of HRSG units. In cases where higher temperatures are not able to be provided, blend filling the solvent and longer contact times (e.g., minimum of 20 hours) sometimes have been used to effectively compensate for the reduced activity of organic solvents at lower temperatures. As a result of the higher temperature requirements, more extensive measures may be needed to provide sufficient heating during the cleaning.

1.7 Results and Lessons Learned

Results of the operational cleanings considered by the project team were highly variable. As indicated earlier, some of the problems were attributed to the much more adherent nature of operational deposits, which could not be removed by the cleaning procedures that had become customary for preoperational cleanings. However, unless videoscopic inspection of tubes and/or tube sampling are performed to demonstrate that the cleaning was in fact successful, it is not possible to definitively state that the preoperational cleaning was uniformly effective in cleaning waterside surfaces.

The available operational cleaning database clearly indicates that there have been both successful and unsuccessful operational chemical cleanings. It is believed that the experiences of the plant facilities addressed by this assessment as presented herein will prove useful to other operators considering their past and future practices relating to HRSG cleanliness assessments and operational cleanings.

In view of the limited attention given to waterside condition assessment, it is suspected that a number of facilities are unknowingly operating with significant deposit accumulations and/or active corrosion sites. The risks associated with heavy deposits and active corrosion cells in

HRSG tubes warrant greater monitoring of unit cleanliness and prompt scheduling of operational cleanings to restore the units to a clean and passive condition.

Subsequent sections of this report provide case studies and highlights from other facilities relative to deposition in and operational cleanings of HRSG units. Lessons learned from evaluation of the cleanings at these various facilities are presented to advance the state of operational HRSG cleanings.

1.8 Reference

1. *Heat Recovery Steam Generator (HRSG) Chemical Cleaning Guidelines*, EPRI, Palo Alto, CA: 2003. 1004499.

2 CHEMICAL CLEANING CASE STUDIES

2.1 Overview

Table 1-1 provided a tabular summary of the facilities for which operational deposits or cleaning experience was considered relevant to the current project. Section 1 presented a general discussion of this experience. A select number of case studies were selected for more detailed discussion of deposition, unit design as it relates to chemical cleaning considerations, and cleaning experience. For each of the selected case studies presented in this section of the report the facility chemically cleaned one to four HRSG units.

In several of the case studies presented, preoperational deposits not removed during HRSG commissioning were indicated to be a contributing factor to the decision to operationally clean. For those facilities in which harmful deposits were detected in the HRSG units within the first year of service, the HRSG manufacturer, and/or general contractor sometimes worked with the owner to resolve responsibility and deposit removal issues. To avoid providing a misleading indication of units which have had residual preoperational deposits or have been subject to subsequent operational deposits, reference to specific HRSG manufacturer organizations in the case study presentations has been withheld.

The case study database summarized in Table 1-1 includes HRSGs from at least eight different manufacturers. Thus it is very clear that problems with HRSG deposition, deposit related damage and cleaning are not unique to one or even a small number of manufacturers or designs. It is considered very likely that equipment from other HRSG manufacturers have had comparable experiences and that these events were not captured when assembling the database. Also, HRSG cleanliness at the end of commissioning is dependent on a number of factors, many of which are beyond the control of the manufacturer. Included here is the approach taken to preoperational cleaning following installation at the plant site. This also supports the view that it is incorrect to presume that the equipment from any individual supplier is immune to problems such as those encountered by the case study population.

2.2 Case Study 1: Chelant Cleanings of Triple-Pressure, Drum-Type HRSG Units

2.2.1 Unit Design

Two triple pressure (1940/480/70 psig or ~13380/3310/480 kPa), drum-type HRSG units were cleaned at the facility characterized by this case study. The facility had two HRSG units supplying steam to one steam turbine (i.e., a two-on-one design). It was a closed cycle design with no export steam or process condensate. The HRSG units operated with duct burners. Cycle makeup was demineralized water. No condensate polishers were provided. The condenser contained titanium tubes and no leaks were reported during operation.

2.2.2 Operational History and Reason for Cleaning

The harps arrived at the construction site wet (they contained some glycol solution) and were immediately lifted into position. A rusty solution drained out when they were lifted for assembly. The units sat open to the air for about one year after assembly due to a construction delay, and then for about six months under a nitrogen blanket following hydrostatic testing. Only a mild detergent cleaning was performed prior to operation. The units were placed in intermittent service for about two months for steam blowing, commissioning, and a brief period of operation. Afterward, tube failures were experienced.

Metallurgical analyses found that extensive microbiologically influenced corrosion (MIC) and out-of-service oxygen pitting had occurred. The MIC confirmed that much of the damage occurred before operation. However, the transport of corrosion products from the economizers to the high pressure (HP) evaporators may have added to overall deposit accumulations during service. Also, the tubercles established prior to service left the units vulnerable to subsequent corrosion and cracking in the corroded areas. The deposits in the initial tube failures were dense and very adherent. Following the tube failures, the units were operated without duct burners for about one-half year before chemical cleanings were performed.

The basic steam/water cycle chemical treatment program consisted of ammonia and carbohydrazide to the feedwater supplying the low pressure (LP) evaporator and trisodium phosphate to the HP and intermediate pressure (IP) evaporator drums. During the fairly limited operating period before the operational chemical cleaning, high ammonia and carbohydrazide feed rates and air inleakage contributed to elevated cation conductivities from carbon dioxide. There were indications that the feedwater dissolved oxygen levels were not optimally controlled. However, the period of operation was sufficiently limited that feedwater dissolved oxygen was not considered to be a primary contributor to HRSG tube deposits.

EPRI normal operating cycle chemistry targets were not able to be maintained during the short (two months), intermittent operating period. Indications of phosphate hideout were noted in the chemistry data, but acid phosphate corrosion was not detected in any of the tube samples analyzed. Neither were there any other indications of chemistry conditions which should cause

significant corrosion in the evaporator sections. The drum blowdown samples generally contained significant iron during operation before the chemical cleanings. Following the chemical cleanings, iron was no longer detected in blowdown samples.

After two months of operation, HP evaporator tube failures were experienced in both HRSG units. This prompted visual inspections, videoscopic inspections, and tube sampling. All failed tubes were replaced with new tube sections. The HRSG units were chemically cleaned about four to five months after the tube failures were first detected (six to seven months of total operation).

2.2.3 Evaluating Deposits and Cleaning Requirements

Extensive videoscopic inspections were made and tube samples collected before the chemical cleaning. Tubes were subjected to deposit weight evaluation, dimensional assessment, and deposit composition analyses. Deposit weights were determined by the mechanical method of deposit removal. Maximum deposit weights detected before the cleaning were 88 g/ft² (~95 mg/cm²), 17 g/ft² (~18 mg/cm²), and 18 g/ft² (~19 mg/cm²) in the HP/IP/LP evaporators, 29 g/ft² (~31 mg/cm²) in the HP economizer, and 28 g/ft² (~30 mg/cm²) in the IP superheater.

Average deposit compositions consisted primarily of steel corrosion products with a small amount of carbon and traces of other miscellaneous metal oxides, phosphorus and sulfur. No indications of acid phosphate corrosion were noted.

2.2.4 Cleaning System Design

Tubes in the economizers, evaporators and LP and IP superheaters were found to contain heavy deposit accumulations and pitting and required cleaning. However, the HP superheaters and reheaters did not require cleaning. This necessitated maintaining a vapor space in the HP steam drums to avoid having the cleaning solvent enter the HP superheaters. The following discussion focuses on the HP evaporator cleaning system design.

2.2.4.1 HP Evaporator Cleaning System

Figure 2-1 presents the cleaning system design used for the HP evaporator section. Orifice plates were installed in the two main downcomers to minimize the amount of flow bypassing the evaporator tubes by passing through the downcomer pipes. The two downcomers run down the sides of the HRSG and then under the HRSG where they connect to form a combined horizontal downcomer. This is referred to as the common lower header herein. Three longitudinal headers are fed from the common lower header. Each longitudinal header feeds five harps of tubes provided by separate feeder pipes of varying diameter.

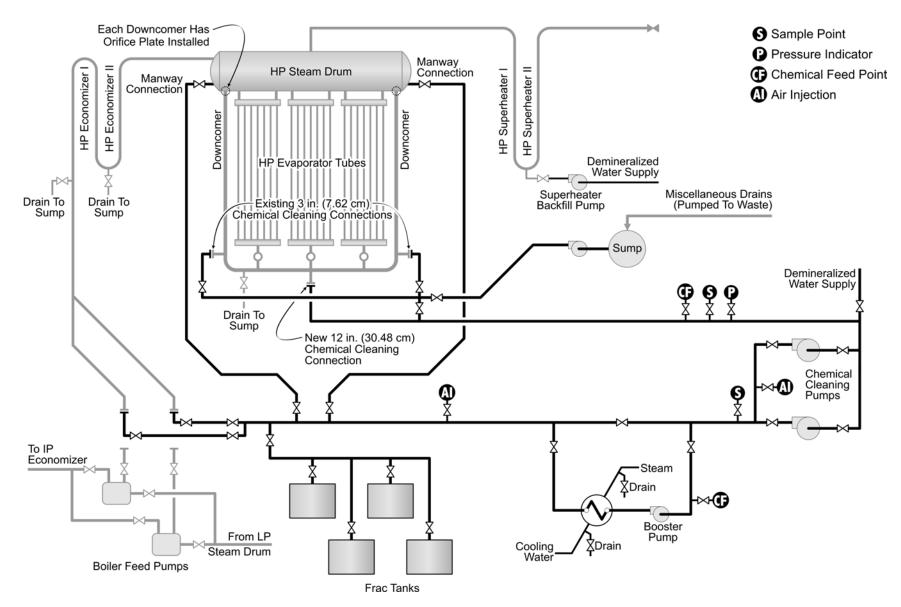


Figure 2-1 Case Study 1: HP Evaporator-Economizer Cleaning

In addition to the two existing (3-inch or ~8 cm diameter) connections, a 12-inch (~30 cm) diameter connection was installed on the common lower header for the three suction connections from the HP evaporator. This new 12-inch (30 cm) diameter connection to the common lower header was fabricated to be a permanent HP flange fitting for ease of use on future chemical cleanings. An 8-inch (20 cm) diameter connection also was installed to the manways at each end the steam drum. Figure 2-2 shows an example of this type of connection. These drum adapters worked very well. Also, two 4-inch (10 cm) diameter lines were installed on the HP feedwater lines at the existing boiler feed pump outlet flanges.

The general flow path was from the common lower header (for the HP evaporator), through the external pump, and to two basically parallel injection paths: the feedwater line/economizer and the steam drum manways. Connections to the steam drums (Figure 2-2) were installed to compensate for the high flow rates needed through the evaporator sections, which would have exceeded the maximum allowable flow rate through the economizers. (The HP 2 economizer tubes contained orifices.) The common pump suction and discharge headers were 24 inches (~61 cm) and 20 inches (51 cm) in diameter, respectively. The contractor installed flanged reducers at the pump to suit the smaller pump actually provided.

The calculated flow rate required for an average flow rate in the HP evaporator tubes of 1 ft/s (~0.3 m/s) equated to circulating the entire system volume every 3.25 minutes. The cleaning contractor designed a system to provide a little over half of this flow rate (circulated system every 5.7 minutes). Therefore, if the flow had been uniformly distributed, the average velocity in the HP evaporator tubes would have been about 0.57 ft/s (~0.17 m/s). The actual system turnover rate was slightly less than the contractor's design (turnover of the evaporator volume in ~5.9 minutes, or an average velocity of 0.55 ft/s or 0.17 m/s).

A detailed evaluation of the feeder pipes estimated the range of solvent velocities in the evaporator tubes to be 0.1 to 1.7 ft/s (~0.03-0.52 m/s). The differences in solvent velocity were due to the harp feeder pipe design and the number of rows of tubes in each harp. Since the front (hottest) two rows of tubes (i.e., the first harp) in the HP evaporator section had the largest feeder-area-to-tube-area ratio, a greater proportion of the solvent probably flowed through these tubes during the cleaning. Solvent velocities in the front row evaporator tubes were estimated to have been 1.7 ft/s or ~0.52 m/s. Since the front row tubes typically have the greatest heat flux during operation, they generally have heavier deposits than tubes in subsequent rows. Therefore, the higher solvent velocity in this area during chemical cleaning aids in cleaning those areas with, potentially, the heaviest deposits. However, in the HRSG design addressed in this case study the greater fluid velocity in the first harp is achieved at the expense of the remainder of the harps in the HP evaporator (during both operation and chemical cleaning). The lowest solvent velocity estimates (~0.1 ft/s) were for tubes in the last harp of the HP evaporator, which were supplied by feeder pipes with orifices (present as part of the HRSG design) to control flows.

To ensure a fluid velocity of at least 1 ft/s (~ 0.3 m/s) in all of the evaporator tubes with this particular design unit would have required a flow rate of over 50,000 gpm (>189 m³/min) in a

once-through arrangement or over 30,000 gpm (>113 m³/min) of fluid circulation by flowing down two evaporator bundles and up a third bundle with bypass flow routed to the economizer and steam drum.

This alternative arrangement would have required additional cutting and blanking of parts of the large (16 inch [0.41 cm] diameter) lower header piping as well as the rather large external piping and pumps. Also, the velocities in the feeder pipes would need to be about 50 ft/s (~15 m/s). This is not without precedent, but it is higher than desired for circulating chemical cleaning solvents. Another possible approach which was not investigated for these cleanings is use of gas-induced circulation up the downcomer pipes and down the evaporator tubes. This could be considered for future cleanings of this unit.

While not shown in Figure 2-1, a temporary sightglass was provided on the steam drum for level control. To avoid aeration, a nitrogen pad was maintained on the steam drum (via the normal nitrogen layup system connection) during the iron oxide removal phase of the cleaning. No buildup of hydrogen pressure was noted in the drum during the cleaning. Also, bleed vents were installed on the economizer upper headers to void noncondensable gases during the evaporator fill and the subsequent cleaning process. As is common on HRSG units, the economizers include downflow sections which can become bound with noncondensable gases if not properly vented.

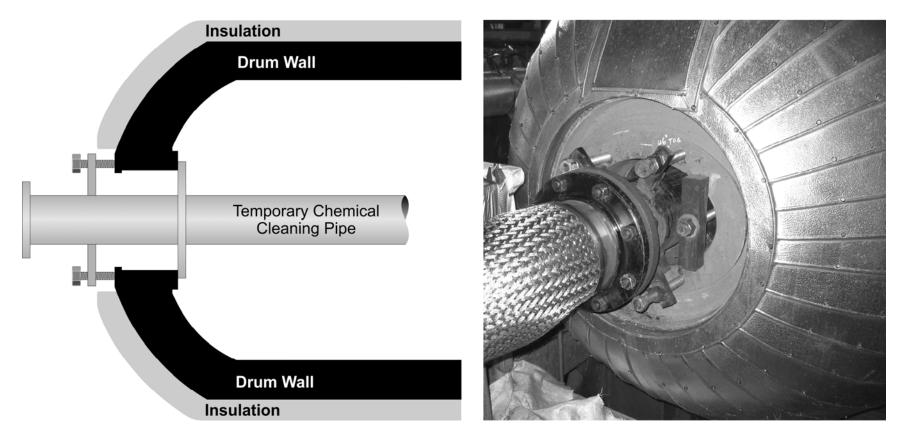


Figure 2-2 Case Study 1: Steam Drum Manway Connection for Temporary Chemical Cleaning Piping

2.2.4.2 IP and LP Evaporator Cleanings

Figures 2-3 and 2-4 depict simplified solvent flow diagrams for the IP and LP evaporator circuit cleanings, respectively. These are discussed briefly in the following paragraphs.

Connections to the lower header for the IP evaporator utilized an existing connection on the downcomer and an additional HP flanged fitting, which was permanently welded to the lower header piping. No drum manway connections were installed. The feedwater line was accessed through the existing flange fittings on the boiler feed pump discharge. The IP superheater was accessed by removing the bonnet and internals from a valve on the IP superheater outlet. The flow path was from the lower header through the pump and heat exchanger, discharging to the superheater and feedwater line.

Connections to the LP evaporator lower header utilized an existing connection on the downcomer plus a new HP flanged fitting which was permanently welded to the lower headers. Connections to the LP superheater outlet and LP feedwater to the LP drum were made by removing the bonnet and internals from existing valves. Accessing the piping through the valves reduced the amount of cutting and welding required on the pressure piping before and after the cleaning process.

The chemical cleaning flow paths for the IP and LP evaporator circuit cleanings included the respective superheaters. The flow path through the superheaters to the steam drum was used in lieu of the steam drum manway flow path indicated for the HP evaporator cleaning. Therefore, the basic flow path was from the bottom header/downcomer with parallel paths to the superheater outlet and feedwater or condensate inlet for the IP and LP drums, respectively. The plan was to monitor the flow rate to each of the flow paths. As indicated later, the goal of proper flow monitoring was not achieved.

2.2.5 Cleaning Procedure and Results

Each of the HP, IP, and LP sections of the two HRSG units was cleaned separately with a solution of diammonium EDTA. Therefore, a total of six separate diammonium EDTA cleanings was completed.

The HP evaporators were cleaned with ~7-9% EDTA (~17-22% as product), and the IP and LP evaporators were cleaned with 3-6% EDTA (7-15% as product). Spent solvent analyses indicated the removal of a substantial amount of iron oxide (0.5-1.5% Fe) and minor amounts of other metals (i.e., 0.002-0.02% manganese and <0.009% of other metals). The spent solvents of typical operational cleanings of conventional boilers contain 0.5-1.0% iron. Solvents which contain higher concentrations of iron (\geq 1%) indicate that the unit was particularly dirty and definitely in need of cleaning.

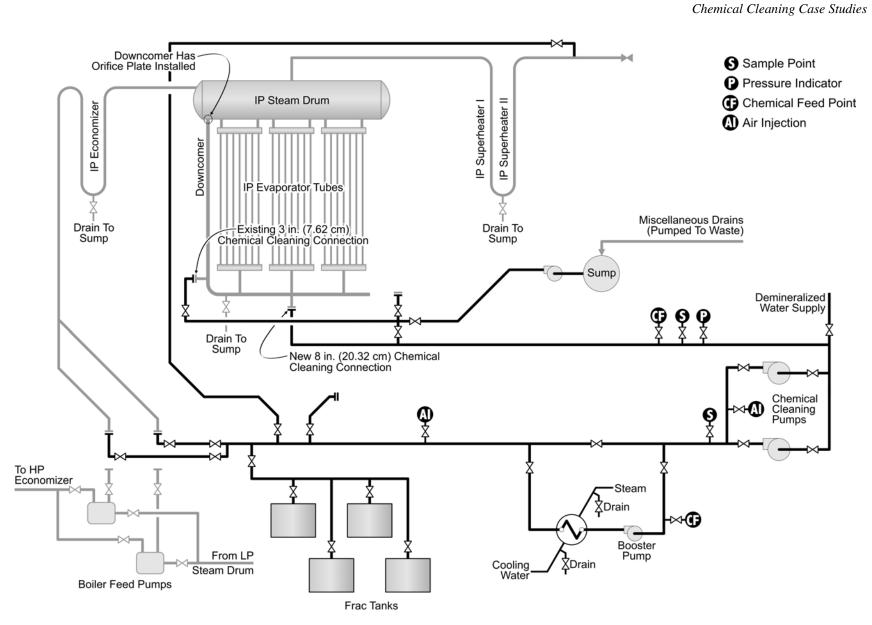


Figure 2-3 Case Study 1: IP Evaporator/Economizer/Superheater Cleaning

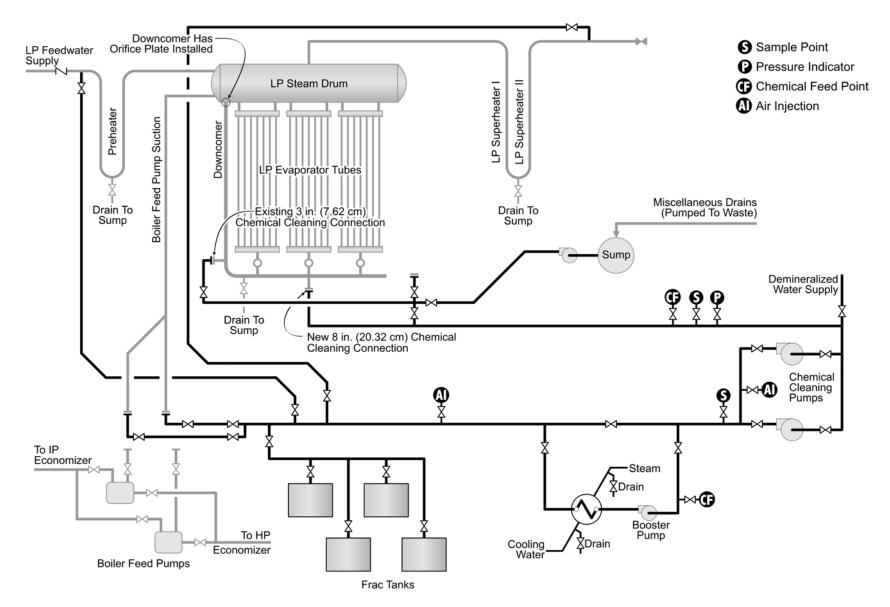


Figure 2-4 Case Study 1: LP Evaporator/Preheater/Superheater Cleaning

After the first HP evaporator cleaning was found to be not completely effective, longer contact times (14-hour iron plateau) were used for the second HP evaporator cleaning in an attempt to compensate for localized low circulation rates. Installation of a removable tube sample loop (for inspection during the cleaning process) was not able to be provided. Solvent temperatures (typically 185-205°F (85-96°C) with a few brief periods below 180°F (82°C) or above 210°F (>99°C) on a couple cleanings) for all six iron oxide removal stages, generally, were at or above the range used for operational cleanings (180-200°F [82-93°C]). A free residual of EDTA was maintained throughout each cleaning process.

Deposit removal was complete in areas known to have good circulation (<0.1 g/ft² residual deposits in areas with 5-20 ft/s or 1.5-6.1 m/s fluid velocity) and was variable in other areas (<0.1 to 11.2 g/ft² in the evaporators). The reduced cleaning performance for some areas also may have been due to elevated solvent pH values during the iron oxide removal phase. The solvent pH readings appeared to be high (>6) during a portion of the iron oxide removal step on two of the six cleanings, and the contractor did not provide formic acid to lower the pH to the normal range (5.0-5.5 measured at 25° C/77°F). The pH readings for at least three of the cleanings were satisfactory for the entire contact period.

Since oxygen was not able to be provided by the contractor, it was originally planned to use sodium nitrite alone for the passivation stage. However, in one instance several additions of sodium nitrite did not appear to be sufficient to complete the passivation process. Air was injected on subsequent cleanings as a supplement to the sodium nitrite. The use of air with sodium nitrite has been standard practice for cleanings of conventional drum type boilers but was not normally required for preoperational cleanings of HRSG units. Since air is mostly nitrogen, the HRSG needed to be vented to control pressures. The higher system pressures during air injection resulted in increased pump seal leakage. Initially, the air injection location was near the pump discharge. It was noted that this injection point seemed to have a greater effect on pump seal leakage than when the air injection location was subsequently relocated to a position farther from the pump discharge.

The quality of the passive layer left after the cleaning process was variable. Since passivation is enhanced by high fluid velocities, some of the variability in the passivation of metal surfaces was attributed to very low fluid velocities in some areas. Poor circulation in some areas also may have contributed to the inadequate and nonuniform distribution of oxidants.

2.2.6 Lessons Learned

- Duct Burners: Dirty HRSG units sometimes can be operated without duct burners, this to reduce the risk of additional tube damage (until the deposits are removed by cleaning).
- Connections: Connections to the lower headers may require permanent changes to the header piping. In addition to existing flanged fittings on the HRSG and feedwater systems, flanged connections can be established to drum manways and through valves on the feedwater lines and steam lines to minimize cutting and welding on high pressure piping and components.

- Hydraulic Conditions Evaluation: Carefully review the HRSG drawings and hydraulic evaluation provided by the cleaning contractor to ensure adequate fluid velocities and solvent distribution during the cleaning.
- Contractor Pump Specifications: Ensure that the contractor provides pumps (including backup pumps) that are designed to handle the temperatures and solvents applied. On these cleanings, both pumps provided by the contractor (rental pumps) were found to be inadequately rated for the cleaning conditions. As a result, the seals experienced rapid, severe failures.
- Use of Troughs; Do not use open-top drain troughs for the discharge of lower header drains as they can overflow and severely limit drain rates. Sealed drain headers are the conventional and preferred for lower header drains. However, open-top troughs can be useful and may be used for viewing and collecting the discharge of vent lines used for bleeding off noncondensable gases.
- Contractor Experience and Qualifications: Use cleaning contractors with extensive experience and a good reputation. The contractor selected for the job did not understand either the basic chemistry of the solvents or the basic chemistry monitoring techniques (pH, EMF, etc.). The contractor did not have the necessary equipment for some tests at the start of the procedure, and the lack of experience with some common cleaning chemicals (oxygen or formic acid) precluded their use for the chemical cleanings.
- Oxidants for EDTA Passivation: For operational EDTA cleanings, it is suggested to ensure that sufficient excess oxidant is available on site and that adequate oxidant distribution can be provided. The EPRI cleaning guidelines provide information for estimation of oxidant doses based on the HRSG volume and the maximum amounts of iron and copper which may be removed. (1) Oxidant distribution is equally important because locally high concentrations of some oxidants (e.g., nitrite) could contribute to transpassive conditions and subsequent corrosion. All chelant cleanings should have the provision to inject some form of oxygen or air for primary or supplemental oxidation.
- Venting: Periodic venting of the upper headers during the preheat (to void air released), iron oxide removal (to void hydrogen), and passivation stages (to void air or oxygen) often is required. This can occur in economizers, superheaters and other circuits which commonly have intermediate upper header supplying sections with downward flow. For example, during the preheat stage for one of the IP HRSG cleanings, no fluid was flowing through the superheater because of an accumulation of noncondensable gases which were trapped in an upper header. Remediation of this condition required detection first (i.e., tube temperature and supply flow monitoring) and then correction (venting).
- Dedicated Flow Meters: Cleaning specifications should require provision of dedicated flow meters for continuous monitoring of all flow rates. The contractor tried to monitor multiple areas by moving a strap-on type flow meter from one location to another. These flow meters can work, but they also can take a while to install, so accurate readings are not immediately obtainable. Also, with some of these units, it is difficult to keep the sensors mounted on 200°F (93°C) piping with standard coupling gels.

- Data Collection Systems: The computerized data collection system used in this case study provided continuous temperature trends for tubes and all other components of the HRSG in the cleaning system. This was invaluable in evaluating the effectiveness of establishing metal temperatures and solvent distribution within the HRSG during preheating and the subsequent cleaning process. This should be standard practice for all operational cleanings.
- Heat Exchanger Capacity: The heat exchanger provided for this cleaning was not sufficiently sized to enable full flow through the heat exchanger. Instead, it was installed with a bypass line such that flow through the heat exchanger was controlled by the bypass valve. During initial heating, the rate of heat increase was limited by the inability to pass all flow through the heat exchanger. As the bypass valve was closed, pump discharge pressure increased and flow rate decreased. To compensate for this, a booster pump was subsequently provided to force solvent through the heat exchanger. The lesson learned is to provide a heat exchanger and associated piping which are large enough to accommodate the desired flow rate.

2.3 Case Study 2: Chelant Cleaning of Dual-Pressure, Drum-Type HRSG Unit

2.3.1 Unit Design

A dual-pressure, drum-type HRSG was cleaned in this case study. The 113 MW unit design had a single HRSG supplying steam to one steam turbine (i.e., one on one design). It was a closed cycle design with no export steam or process condensate. The cycle received demineralized water makeup and no condensate polishers were present.

2.3.2 Operational History and Reason for Cleaning

The unit was placed into commercial operation in 2001 with a total of 17,423 operating hours before the chemical cleaning. The only preoperational cleaning was an alkaline flush for grease removal.

In 2005, turbine pins came loose and punctured the titanium condenser tubing, resulting in a massive cooling water leak. No evaporator tube samples were removed for analysis before the chemical cleaning. The facility used the 2003 EPRI guideline for chemical cleaning of HRSG units to determine the need to proceed with chemical cleaning of the unit.⁽¹⁾

For a little over a year, the condensate/feedwater for the unit was treated with diethyl hydroxylamine (DEHA) and ammonia, and the boiler water was treated with trisodium phosphate. The steam/water cycle chemical treatment program was subsequently converted to all volatile treatment (AVT) without any reducing agent (i.e., now feed only ammonia). EPRI normal operating cycle chemistry targets for AVT(O) were maintained during the remainder of the operating period, leading up to the condenser leak. ^(2,3) This treatment program has been continued since the chemical cleaning as well.

2.3.3 Evaluating Deposits and Cleaning Requirements

As stated previously, no tube samples were collected for deposit weight, dimensional assessment and deposit composition analysis before the chemical cleaning. The reason for the chemical cleaning was to remove hardness (calcium and magnesium) salts and iron deposits from the waterside surfaces.

Diammonium EDTA was selected as the cleaning solvent for the following reasons.

- Diammonium EDTA solutions are sufficiently acidic (pH 4.5 to 6.0) to dissolve scale and deposits from generating tube waterside surfaces.
- The removal of iron oxide deposits from waterside surfaces can proceed to completion in the temperature range of 150-200°F (~66-93°C).
- The solvent can be circulated at elevated velocities without being corrosive to metal surfaces.
- The solvent has no maximum contact time restrictions. Analytical results for percent iron and residual EDTA are used to determine the length of the cleaning.
- The quantity of waste from the chemical cleaning is reduced, since the same solvent can be used both for scale and deposit removal and system passivation (with the addition of ammonia and oxidant).

The preceding list of reasons provided by the facility deserves a few comments.

- Field experience indicates that the dissolution rate for iron may decline at pH values above pH 5.5
- Temperatures below 180°F (~82°C) result in slower removal of operational deposits and may require extended contact times.
- While EDTA can be safely circulated for extended periods and is much less corrosive than circulated hydrochloric acid, the circulation of EDTA solutions at excessive velocities may result in elevated corrosion rates. The authors are not aware of any documented cases to date where high velocities were the cause of high corrosion rates in otherwise properly applied EDTA solutions. However, it is cautioned that failure to conduct a suitable hydraulic analysis of the HRSG system to be cleaned could result in sufficiently high velocities to increase corrosion activity of EDTA solvents.

2.3.4 Cleaning System Design

Figure 2-5 presents the cleaning system design used for the unit. Downcomers for both the HP and LP evaporators were connected to a temporary suction pipe supplying the diesel-powered chemical cleaning pump. Cleaning pump discharge flowed through a heat exchanger before splitting into parallel paths to the HP and LP economizers. The measured flow rate to the HP economizer was 275 gpm, and that to the LP economizer was 342 gpm with both drum levels holding constant. The system volume was 24,000 gallons. The calculated velocities in the evaporator and economizer tubes during the cleaning were not reported. The estimated turnover

rate for the system was 39 minutes, which is much lower than was determined in the Case Study 1 cleaning.

2.3.5 Cleaning Procedure and Results

The HP evaporator and LP evaporator were cleaned with approximately 3.3% EDTA (8.2% product). The spent solvent analyses indicated the removal of 0.388% iron (777 lbs/ 353kg Fe) and minor amounts of other metals (i.e., 23.3 lbs/10.6 kg calcium and 4.2 lbs/1.9 kg magnesium). Typical operational cleanings of conventional boilers contain between 0.5% and 1.0% iron in the spent solvents. Therefore, either this HRSG was not particularly dirty as a result of the chemistry upset or not all of the deposits were removed. Since no preoperational cleaning was completed, it is expected that mill scale deposits remaining after unit commissioning were removed during the chemical cleaning process. Therefore, the chemical cleaning was successful in reducing both old and new deposition and scale, which otherwise could have jeopardized HRSG tube integrity.

During the EDTA iron oxide removal stage of the cleaning, the cleaning contractor was monitoring the solvent iron and available EDTA concentrations (see Figure 2-6). The station terminated the EDTA iron stage after the iron and available EDTA concentrations were steady for six hours. Upon further inspection of the available EDTA concentration data, the available EDTA concentration was still trending downward at the termination of the EDTA iron stage.

During an EDTA chemical cleaning, a useful tool for interpreting analytical data is performance of an EDTA mass balance. The EDTA mass balance accounts for the EDTA combined with iron and other deposit constituents plus the available (unreacted) EDTA in the solvent. The accepted industry standard for the quantity of EDTA combined with the iron in solution is 5.23 lbs (or kg) of EDTA for every pound (or kg) of iron. The equation for EDTA mass balance is as follows.

Total EDTA (lb or kg) = % Available EDTA + % Iron x 5.23 (lb or kg) Equation 2-1

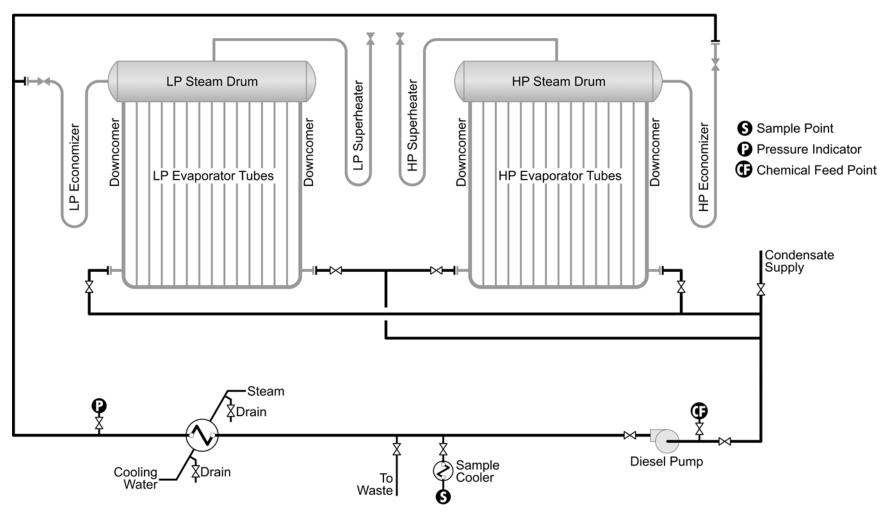


Figure 2-5 Case Study 2: Cleaning System Design

As shown in Figure 2-6, the trends for both the percent available EDTA and percent total EDTA indicate that the EDTA was not completely distributed throughout the HP and LP evaporators. It is hypothesized that this trend may have been due to insufficient dispersion of EDTA in the system. Figure 2-7 shows the amount of system volume which would have contained EDTA, assuming the EDTA and iron concentration data were correct. It is possible that portions of the HRSG did not contain an equivalent amount of EDTA until the last one to two hours of the iron oxide removal stage. The other possible problem with the EDTA data could have been the test procedure for available EDTA concentration. After the solvent pH was elevated above 9.1 with ammonia for the passivation stage, the available EDTA concentration value was 1.5%. Using an iron concentration of 0.35% at the completion of the iron stage and 1.5% available EDTA, the total EDTA concentration would be 3.33% - which would correspond to the expected original concentration of EDTA added to the system. The high free and total EDTA concentrations may have been due to an error in EDTA readings during the iron oxide removal stage. It is also possible that the lower EDTA concentration represents more uniform dispersion of the EDTA by the end of the passivation stage. This case study was a demonstration of the potential benefits of calculating and tracking the total EDTA concentration during the cleaning, assessing solvent distribution, and determining the end of the cleaning process.

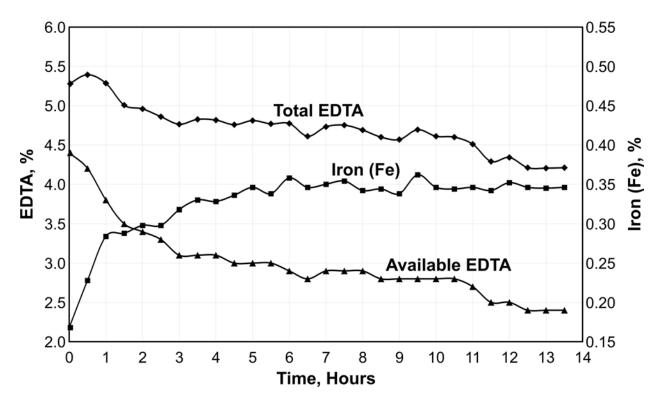
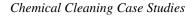
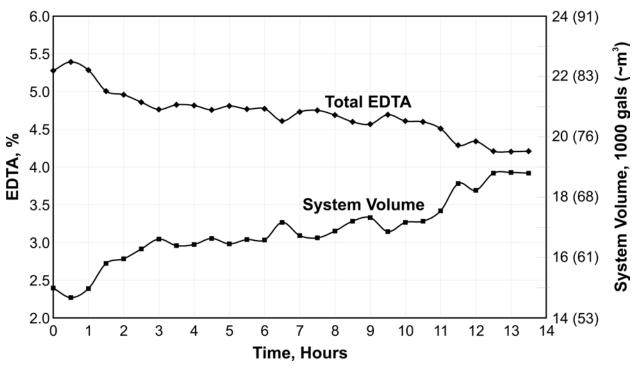


Figure 2-6 Case Study 2: Iron Oxide Removal







For diammonium EDTA chemical cleanings, it is advised to maintain solvent pH nearer to the acidic level (5.0 to 5.5) for optimal scale and deposit removal. Figure 2-8 shows solvent pH data during the iron oxide removal stage of the cleaning. Solvent pH gradually increased from 5.6 to 5.9 during the iron oxide removal stage. To maintain the same rate of iron oxide removal, formic acid should have been injected into the cleaning solvent to reduce the solvent pH back to a range of 5.5 to 5.6. Alternatively, longer contact times may have been required to ensure that chemistry had stabilized and the cleaning stage was complete. This case study is considered to be a clear demonstration of the need to ensure that a supply of formic acid is on hand to reduce the pH if required.

2.3.6 Lessons Learned

- Calculate and Track Total EDTA. Tracking the total EDTA (based on free EDTA and metals dissolved) is recommended for all EDTA cleanings to evaluate when the solvent is properly distributed and consumption has ceased (see Figures 2-6 and 2-7).
- Diammonium EDTA pH Control. The rate of iron oxide removal decreases as the pH rises. With this solvent it is desirable to maintain pH values of 5.0-5.5 for optimal iron oxide removal.

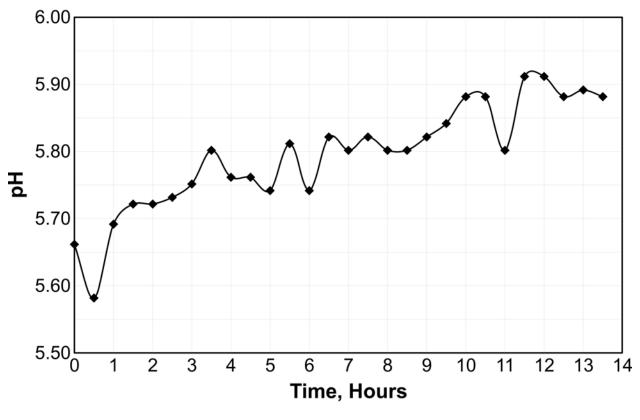


Figure 2-8 Case Study 2: Solvent pH During Iron Oxide Removal

2.4 Case Study 3: Cleaning of a Dual-Pressure Drum-Type Evaporator with a Citric/Phosphoric Acid Mixture

This case study was selected to serve as an example of the cleaning performance with weak solvents and poor circulation for some HRSG facilities. Failure to properly specify the types and quantities of solvents and procedures can result in an unsatisfactorily cleaned HRSG.

2.4.1 Unit Design

Two dual-pressure HRSG units with 1400 psig (9.7 MPa) HP drums were cleaned after fairly brief operation due to operation with exhausted makeup demineralizers. The units were part of a cogeneration facility for a refinery. The HRSG units had duct burners.

2.4.2 Operational History and Reason for Cleaning

A nominal preoperational cleaning was performed on the units using a mild surfactant/detergent solution at a pH of 6.0-7.0 and temperatures of 40-120°F (4.4-48.9°C) followed by a cleaning solution to remove iron composed of citric acid and phosphoric acid. This same mixed acid solvent was used for the operational cleaning as described herein. The unit was placed in service

and run for approximately 100 hours with exhausted demineralizers. The HRSGs essentially ran with untreated lake water as makeup during this period of time.

2.4.3 Evaluating Deposits and Cleaning Requirements

No visual or videoscopic inspections were performed, and no tube samples were collected.

2.4.4 Cleaning System Design

Following flushing with ambient temperature water, a chemical cleaning was performed. Since the upset occurred shortly after startup, the facility elected to use the same contractor, equipment, connections, and procedures used for the preoperational cleaning. Figure 2-9 is a simplified diagram of the HRSG and associated cleaning circuit. While the HRSG was designed with 6-inch diameter (15 cm) connections on the lower evaporator headers, these were decreased to 4-inch (10 cm) diameter connections for attachment to the chemical cleaning contractor's pumps. The flow path was from the lower headers (via 4-inch or 10-cm connections) of the HP (one front right side connection) and LP evaporators with discharges to the feedwater lines (3-inch or 7.6 cm diameter connections) to each HRSG and the main steam line safety valve. A 6" x 4" pump (15 cm x 10 cm) was provided for circulation by the contractor.

While not apparent in Figure 2-9, the HRSG actually had two of every header and tube set shown in the drawing. As viewed from the combustion turbine exhaust, there would be duplicate left-hand side and right-hand side headers. However, there was only one HP evaporator steam drum and one LP evaporator steam drum. Therefore, in addition to the connections noted earlier, there was a discharge of solvent from the heat exchanger to the left back lower HP evaporator header with the return from the right front lower HP evaporator header. With orifices in the downcomers in the steam drum (although there was no confirmation that the downcomers were, in fact, orificed), the solvent flow would have been forced up the HP evaporator tubes on the left-hand side, through the steam drum, and back down the HP evaporator tubes on the right-hand side of the HRSG. Incidentally, the lower HP evaporator headers did not contain division plates. Therefore, all seven of the lower HP evaporator headers on one side of the HRSG were interconnected by feeder pipes.

No flow meters were included in the cleaning circuit. However, the line sizes and the pump size indicated that the maximum possible circulation rates (<1000 gpm or 227 m³/hour) would have been a fraction of the flow rate required per section to achieve the typical fluid velocity goal of 1 ft/s (0.3 m/s) in the HP evaporator tubes. Table 2-1 provides a simplified summary of the estimated flow rates which would have been required for the HRSG sections. Calculations indicated that it would have been possible to use the existing fittings to effectively clean the feedwater heater, economizers, and superheaters. However, effectively cleaning the evaporators with an organic solvent would have required larger pumps and changes to the evaporator connections.

As indicated in Figure 2-9, the HRSG features primary and secondary economizer stages. Since tube dimensions and the number of tubes were not the same in each stage, the velocity in the economizer stages in series will vary. This applies to the other major circuits (evaporators, superheaters, feedwater heaters) as well. In this particular design, velocities within a basic circuit varied by about 50% from the highest to the lowest. These flow calculations were completed after the cleaning and were not incorporated into the cleaning system design by the cleaning contractor

A possibly improved design for future cleaning of this HP evaporator would involve attaching the temporary piping system to all four (front and rear left and right sides) flanged cleaning connections (provided by HRSG manufacturer) on the lower headers of the HP evaporator. Flow to and through the superheaters, economizers, and wash water sections could discharge to the steam drum and supply some of the solvent flow required by the evaporators. However, as indicated in Table 2-1, the additional flow to circulate the evaporators is much greater than the flow rate needed to clean the other components. Theoretically, the additional flow could be provided by increased flow rates through these other components, flowing up one side of the HP evaporator tubes and down the other side - and possibly by providing connections to the steam drum manways (as discussed in Case Study 1).

2.4.5 Cleaning Procedure and Results

While not involved in the planning process, a consultant was contacted by one of the parties involved to view the chemical cleaning. The cleaning solution was a proprietary blend of citric acid, phosphoric acid and inhibitor. After dilution to the concentration recommended in the product literature, the pH should have been 0.6-1.0. The material safety data sheet (MSDS) indicated that the applied solvent contained 0.14-0.19% citric acid, 0.05-0.09% phosphoric acid, and 0.01-0.02% inhibitor. This blend of solvent provided minimal iron removal capability. No iron concentration testing was performed (the cleaning contractor tested only for pH and acid content). The temperature desired and maintained during the cleaning was not noted. However, the solvent was so dilute that the cleaning could not have been effective.

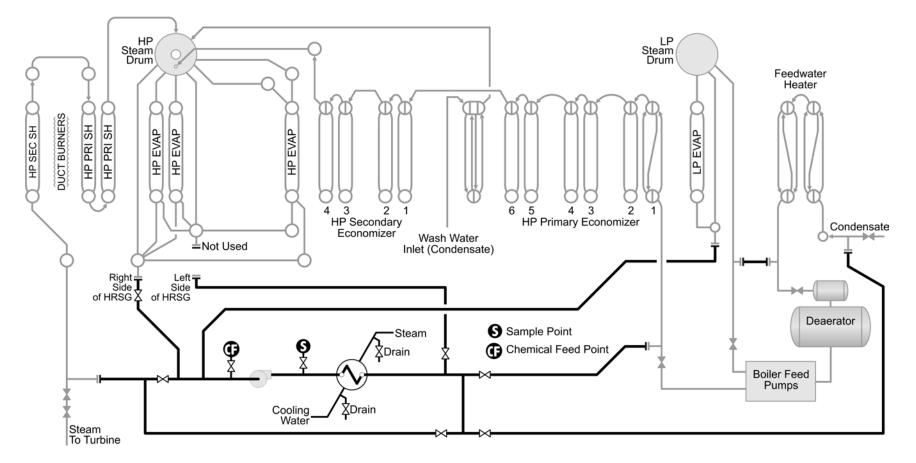


Figure 2-9 Case Study 3: Simplified Drawing of HRSG Cleaning System

Area Circuit	Minimum Flow Per Side (c)	
	1 ft/s, gpm	0.3 m/s, m³/hour
Evaporator ^(a)	975	221
Feedwater Heater ^(a)	283	64
Additional Circulation Needed For LP Evaporator (No LP Superheater)	692	157
Evaporator ^(a)	4,319	981
Economizer ^(a)	245	56
Wash Water	82	19
Superheater ^(a)	462	105
Subtotal Without Evaporator	789	179 ^(b)
Difference (Additional Circulation Needed For LP Evaporator	3,530	802
v rate, some of the in-series sections of this circuit wo	ould be above 1 ft/	s (0.3 m/s) to ensure
	Feedwater Heater ^(a) Additional Circulation Needed For LP Evaporator (No LP Superheater) Evaporator ^(a) Economizer ^(a) Wash Water Superheater ^(a) Subtotal Without Evaporator Difference (Additional Circulation Needed For LP Evaporator v rate, some of the in-series sections of this circuit we the minimum velocity in all tubes.	Evaporator (a)975Feedwater Heater (a)283Additional Circulation Needed For LP Evaporator (No LP Superheater)692Evaporator (a)4,319Economizer (a)245Wash Water82Superheater (a)462Subtotal Without Evaporator789Difference (Additional Circulation Needed For LP Evaporator3,530V rate, some of the in-series sections of this circuit would be above 1 ft/

Table 2-1Case Study 3, Simplified Summary of Hydraulic Evaluation

^(b) Rounding errors account for the differences in subtotals in m³/hour.

^(c) Since there are two sides of the HRSG, total cleaning flow rates would be twice these values.

2.4.5.1 Postcleaning Deposit Evaluation

A videoscopic inspection of the evaporator and primary superheater was performed after the chemical cleaning. A nonuniform oxide layer and loose oxide was apparent on all evaporator and superheater surfaces examined, and an apparent scale layer was noted on the evaporator tube surfaces.

A few days after cleaning a 1.5-2.0-inch (3.8-5.1 cm) wide by 0.25-inch (0.6 cm) thick accumulation of white/tan deposit material was collected from an HP Evaporator lower header for analysis. Initial analysis determined the deposits to be 70% organic and 30% iron. The white crystalline material left on tube surfaces following the cleaning was analyzed by X-ray fluorescence for elements, and FT-IR, liquid chromatography, and C-13 NMR thus determining that the deposits remaining were triferrous dicitrate decahydrate. Extensive testing was performed by another laboratory because there was some concern that the deposits might have been associated with polyacrylates from the on-site chemical treatment vendor's dispersant formulation used in the HRSG evaporators. In addition to analyses showing that the organic portion was citrate, tests were performed by gas chromatography to show that this material was not the dispersant used to treat the HRSGs during service.

About one month later, and after additional water flushing, the tubing was videoscopically inspected again. The pictures were of very poor quality, but it appeared that sludge and scale were still present. The photographs were of the primary superheater tubes, the lower headers for the primary superheater tubes, and the evaporator tubes. Evaporator tubes were accessed remotely from the steam drum (through the riser pipes to the steam drum).

After a weld failure (caused by defective workmanship) about five months following the latter inspection, the videoscopic inspection was repeated and moderate scale was again noted on evaporator tube surfaces. Inspection findings concluded that the unit appeared dirty and that another chemical cleaning was possibly required. However, no additional cleaning was performed at that time. The unit was reportedly experiencing rather severe hideout following the cleaning; phosphate residuals reportedly decreased to 0.1 ppm when the duct burners were placed in service. When the unit was drained and refilled, the measured phosphate concentration was over 50 ppm with a boiler water pH below 8.3. These classic indicators of hideout and return suggest that this unit was possibly on the road to tube damage and failure from acid phosphate corrosion.

2.4.6 Lessons Learned

- Hydraulic Evaluation: Perform a hydraulic evaluation when planning the cleaning to verify that connections, pipe sizes, and pump capacities are sufficient to provide the required velocities for the solvent in all circuits.
- Consider Cleaning with Mineral Acids: For some HRSG designs, the use of solvents (e.g., inhibited hydrochloric acid) and procedures (e.g., blend/filling) which do not require continuous circulation may represent the preferred approach for operational cleaning. The specific solvent recommended for consideration in this case would have been inhibited hydrochloric acid.
- Properly Evaluate Proprietary Solvents: If proprietary solvent formulations are considered, obtain samples of the product in advance and evaluate the proposed cleaning formulation and conditions for cleaning effectiveness with the aid of tube samples. In this case study, dilution of the product rendered it virtually useless.
- Citrate Precipitation: As indicated in the EPRI guidelines ⁽¹⁾, the application of insufficient citric acid and/or localized spending of the solvent can result in precipitation of iron citrate.
- Incomplete Cleaning/Hideout after Cleaning: Phosphate hideout was noted in this HRSG unit, in which residual deposits were left behind due to inadequate chemical cleaning.
- Flow Meters: Install in-line flow meters to reliably monitor solvent flow rates in individual system flow paths.
- Experienced Contractor. Use a chemical cleaning contractor with experience in planning and performing operational chemical cleanings.

2.5 Case Study 4: Planning for Cleaning of a Once-Through HRSG Unit

While less common than drum type HRSG units, once-through HRSG units also accumulate deposits requiring chemical cleaning. A limited case study is presented herein covering the planning and cleaning design for operational cleaning of a once-through steam generator. Complete details are unavailable as the author familiar with the planning activities was unavailable for the field cleaning, and data collected during the cleaning process were not available.

2.5.1 Unit Design

The once-through HRSG had a 1500 psig (~10 MPa) HP evaporator section and a 20 psig (~140 kPa) LP evaporator section. No drums were provided in the design. The evaporator tubes were high nickel alloys, as were the inlet headers (Alloy 800 and/or Alloy 825). However, the steam outlet headers were composed of P22, a low alloy steel (~2% chromium/1% molybdenum). Hot gas discharge from the combustion turbine enters the HRSG from the bottom and flows up through the HRSG.

2.5.2 Operational History and Reason for Cleaning

No preoperational cleaning was performed on the unit. After about two years of operation, silica and iron deposits were found on the turbine and some overheating was reportedly detected in the HRSG. The source of the silica could not be determined from available operating data, thus the possibility existed that it may have been introduced during HRSG fabrication and erection activities.

2.5.3 Evaluating Deposits and Cleaning Requirements

In consideration of the high nickel alloy tubing used in this HRSG design, cleaning with an organic solvent was required. Solvents considered included hydroxyacetic/formic acid, EDTA, and ammoniated citric acid. These options were reviewed with the HRSG manufacturer and presented to the owner. Proposed use of hydroxyacetic/formic acid and EDTA solvents was rejected by the owner because the cleaning wastes could not be disposed of on site. Use of a citric acid base solvent was preferred by the owner as it could be disposed of on site. Also, use of this solvent was the option preferred by the HRSG manufacturer.

No tube samples were collected or provided before the cleaning to assess deposit weight or deposit composition or to perform a laboratory cleaning evaluation. Based on the turbine deposit composition indicated earlier, the cleaning contractor proposed to perform a cleaning using 3.0% citric acid with 0.31% ammonia, 0.25% ammonium bifluoride, and 0.2% of a common commercial inhibitor. Inclusion of the ammonium bifluoride was felt to be needed for dissolution of silica; this conclusion was based on silica analysis results for the turbine deposits.

The passivation stage of the cleaning was to involve the addition of sufficient ammonia to raise the solvent pH above 9.5. The oxidant to be used for passivation was not specified in the contract documents and other available records.

2.5.4 Cleaning System Design

As shown in Figure 2-10, the HP and LP sections were cleaned in parallel. Flow followed the normal service path through each steam generator (which was from the top to the bottom of each evaporator section). The preheater or LP economizer section, located above the LP evaporator, was not part of the cleaning solvent flow path and are not included in the drawing. The HRSG was fairly compact (only about 30 feet or 9.1 m high).

The cleaning system was designed to provide a fluid velocity of 1 ft/s (0.3 m/s) in all evaporator tubes. This proved to be a little more complicated than expected because the tube diameter increases as fluid flows through each once-through evaporator section.

In order to obtain 1 ft/s (0.3 m/s) in the larger diameter (1.25 inches or 31.8 mm) tubes in the HP section, the velocity in the small diameter tube sections was higher. For example, the velocities in the 0.5-inch (1.27 cm) and 1-inch (2.54 cm) diameter tubes were 8.31 ft/s (2.53 m/s) and 1.55 ft/s (0.47 m/s), respectively. The LP section flow was set at 1.43 ft/s (0.44 m/s) for the largest diameter, which resulted in 8.31 ft/s (2.53 m/s) in the smallest diameter tubes. Fortunately, the length of the smallest diameter tubing was rather short (2-5 ft or 0.61-1.52 m for the LP and HP evaporators). Therefore, the overall pressure drop was not excessive.

As indicated in Figure 2-10, existing connections on the piping system could be used or adapted for use to provide the necessary circulation rates. A hydrostatic test connection and two other existing flange connections provided three of the four needed connections for the operational cleaning. The fourth connection was through a safety valve on the LP superheater outlet.

The contractor cleaning equipment was specified to include a 6 inch x 4 inch (15.4 x 4.2 cm) pump with a minimum flow rate of 450-500 gpm (102-114 m³/hour). The contractor heat exchanger area (conventional shell-and-tube design) was specified to be 500 ft² (46.5 m²).

Utilities provided by the plant for the cleaning included 225 psig (1.55 MPa), 500°F (260°C) steam and demineralized water. The system volume was about 3500 gallons (13.2 m³).

2.5.5 Chemical Cleaning Procedure and Results

While the cleaning was indicated to have been successful, the author contributing his experience for this case study was not present during field cleaning activities and efforts to locate information on the work for this project were not successful.

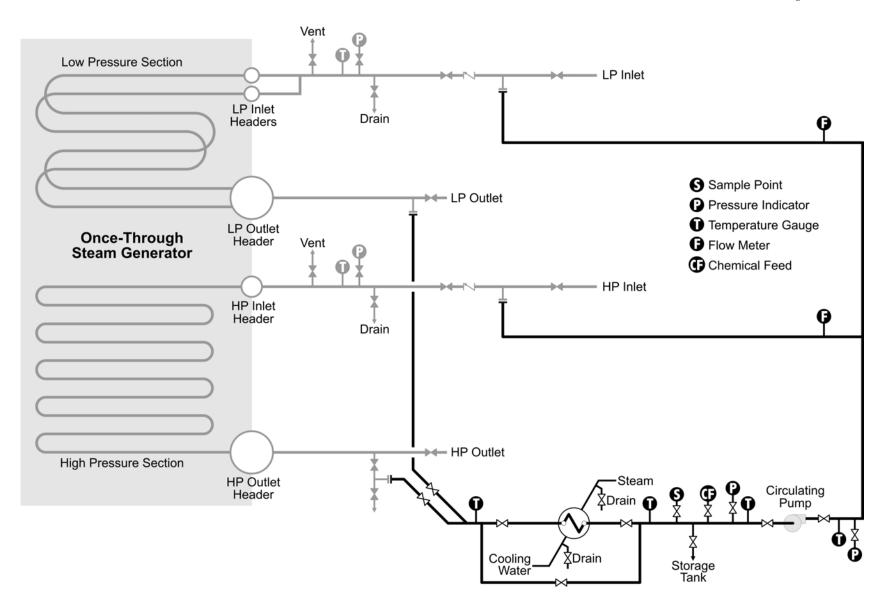


Figure 2-10 Case Study 4: Simplified Cleaning System Schematic

2.5.6 Lessons Learned

- Hydraulic Evaluation: Even though they normally have forced circulation during service, HRSGs with once-through evaporators also require a hydraulic evaluation prior to chemical cleanings as tube diameter increases as fluids pass through the once-through evaporator circuits.
- Solvent/Metal Compatibility: Once-through evaporators can contain more exotic alloys and may require advanced planning or testing to ensure solvent/metal compatibility with some solvent combinations.

2.6 Case Study 5: Hydrochloric Acid Cleaning of Single Pressure HRSG

2.6.1 HRSG Design

This case study features a single pressure HRSG with upper and lower drums to permit access to the tubes. This type of design continues to be installed but is more common at older cogeneration facilities. The drum pressure operates at 600 psig (4.1 MPa). The HRSG has a superheater but no reheater.

As shown in Figure 2-11, a sweet water condenser (SWC) was incorporated in the HRSG design to provide attemperation water. While common in the pulp and paper industry, SWCs are less commonly present in the power industry. A sweet water condenser is a shell-and-tube heat exchanger with feedwater (from the economizer) flowing through the inside of the tubes and saturated steam (from the steam drum) condensing on the shell side. The condensed, saturated steam is sprayed into the superheated steam to control steam temperature.

The materials of construction for the SWC at the facility discussed in this case study were not reported. However, since hydrochloric acid was circulated through the sweet water condenser for the cleaning, the tubes presumably were fabricated of carbon steel or low-alloy steel as most other materials used for sweet water condensers would have been incompatible with this solvent. For HRSG units in cogeneration facilities receiving process condensate, use of SWC technology is worth considering as a way to avoid steam contamination when the process condensate is used for attemperation and the design does not include a condensate polisher to control levels of ionic impurities.

2.6.2 Operational History and Reason for Cleaning

The unit was primarily used for cogeneration. Therefore, it received process condensate return from an industrial facility. Return condensate was treated through an electromagnetic filter to remove the bulk of the suspended magnetite. The unit had a separate spray/tray deaerator in the feedwater system. Water treatment was provided and controlled by a chemical vendor.

Feedwater to the HRSG was treated with a blended product believed to be primarily sodium polyphosphate and caustic. It is thought that neutralizing amines were applied to the feedwater.

2.6.3 Evaluating Cleaning Requirements and Deposits

No tube samples were collected either before or after the chemical cleaning. The owner had a policy of performing cleanings based on a point system which included many points based on operating time. Essentially, a cleaning was required every seven years with the point system in the absence of any other factors to which a significant number of points could be assigned.

In lieu of tube sample deposit evaluations, steam drum and mud drum deposits were collected for analysis. X-ray fluorescence (XRF) analyses indicated that the drum deposits consisted mainly of magnetite (97-99%) with lesser amounts of loss on ignition (1%), pyrophosphate (0-1%), and calcium oxide (0-1%). As will be apparent in the subsequent cleaning discussion, failure to obtain and analyze a tube sample prior to the cleaning resulted in a vast underestimation of deposits present in the HRSG. As a consequence, insufficient solvent was available to ensure that the cleaning was effective.

2.6.4 Cleaning System Design

Initially, the system volume for the economizer (2600 gallons or 9.8 m³) and evaporator (7150 gallons or 27.1 m³) was calculated to be 9750 gallons (36.9 m³) plus 500 gallons (1.9 m³) for the SWC (10,250 gallons total or 38.8 m³). However, the assumed cleaning volume for planning purposes was selected as 7500 gallons (28.4 m³), this based on the field determination of volume from a prior chemical cleaning. Sometimes, estimates from design drawings are refined based on flow or volume measurements during chemical cleanings. A flow meter was included in the cleaning system.

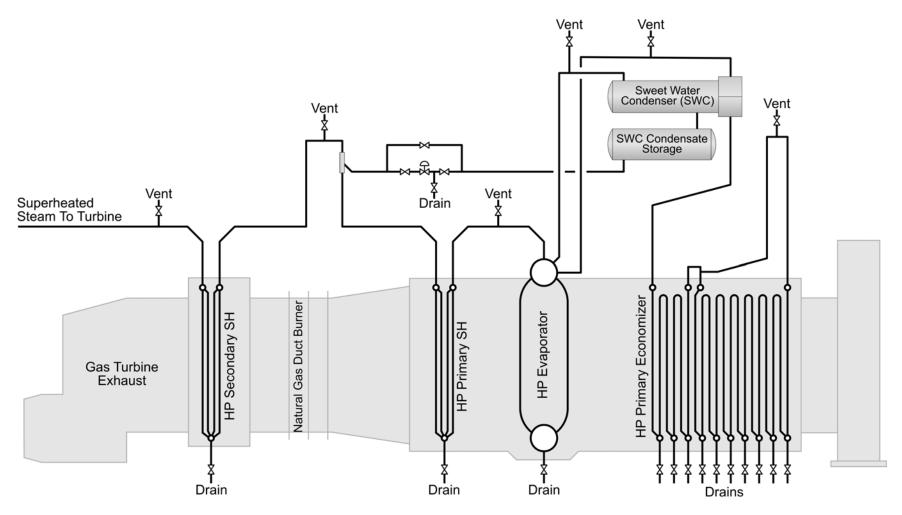


Figure 2-11 Case Study 5: HRSG with a Sweet Water Condenser

2.6.5 Cleaning Procedure and Results

2.6.5.1 Preheat Stage

The HP evaporator was filled to just over centerline and water was circulated using a 4 inch x 3 inch (10.2 cm x 7.6 cm) pump at 385 gpm (~87 m³/hour) through a heat exchanger. The flow path is thought to have been from the mud drum (lower header for evaporator section) to the economizer inlet header (with the economizer outlet flowing through the SWC and discharging to the steam drum). A small rental boiler provided to supply 40 psig (0.28 MPa) steam proved inadequate and it was thus necessary to subsequently run a 2-inch (5.1 cm), 165 psig (1.1 MPa) steam supply line for use during the cleaning.

The superheater was backfilled before starting the acid stage. If superheaters or steam lines are not to be cleaned, they need to be backfilled. During the Case Study 5 HP evaporator cleaning it was determined that two large valves to the condensing turbine were leaking badly. In addition to the initial delays in filling the superheater, the leaky valves required periodically refilling these components during the cleaning process to keep them adequately full or flushed. This balancing of water leakage and replacement water was complicated and could have resulted in dilution of the solvent in the evaporator. In addition to the losses and risks associated with leaky valves during both in-service and out-of-service periods, leaky valves can be a major problem when performing a chemical cleaning. These valves should be inspected and repaired or replaced as needed prior to chemical cleaning.

2.6.5.2 Iron Oxide Removal

An initial solvent sample failed the ampoule-type inhibitor test and additional inhibitor had to be added before starting the cleaning. Acid was subsequently blended into the preheat water in the HRSG while circulating over a two-hour period. Temperatures were maintained at 140-149°F (60-65°C). It did not appear that any calculations were performed to ensure adequate flow rates to provide circulation in the HP evaporator tubes for proper distribution of solvent. Circulation was performed once per hour at 300 gpm (68 m³/hour) for 15 minutes. After 4.5 hours of contact, the HRSG was drained because of very high iron content. The composite drain sample had 2.3% iron and 5.3% hydrochloric acid. Traditionally, hydrochloric acid is drained once the iron concentration exceeds about 2.0% - this to avoid ferric ion corrosion. Therefore, personnel elected to terminate this stage before iron levels stabilized.

The HRSG was rinsed twice with water (filled with rinse water, circulated for 10 minutes, and drained) and then filled with ammoniated citric acid (citric acid at a pH of 3.5) in an effort to remove additional iron. After about four hours of circulation at 140°F (60°C), the solution was drained. The ammoniated citric acid stage was still removing iron (0.49%), but the stage had to be aborted because no additional solvent was on site.

2.6.5.3 Passivation Stage

The system was filled with passivation solution (citric acid with iron, ammoniated to a pH 9.5, and oxidized with sodium nitrite), circulated for three hours and then drained. Copper concentrations collected during the passivation stage ranged from 0.028-0.09%. The total amounts of material removed in the entire cleaning/passivation were estimated to be 2137 pounds (969 kg) of magnetite and 30 pounds (~14 kg) of copper.

2.6.5.4 Postcleaning Activities and Recommendations

A lot of chip scale was found in the tube ends in the evaporator section. It was suggested to flush all residual deposits from the evaporator and economizer sections before returning the unit to service. Since hydrochloric acid was used for the cleaning and acid may be trapped within and beneath residual deposits, acid-laden sludges could contribute to subsequent underdeposit corrosion and hydrogen damage in the HRSG unit. Videoscopic inspection should have been performed after the cleaning to evaluate cleaning effectiveness. Routine tube sampling for deposit weight and composition analyses would be suggested for this unit.

2.6.6 Lessons Learned

Lessons demonstrated in this case study were as follows.

- Collect Tube Samples before Cleaning: While tube sampling was required to assess cleaning requirements according to EPRI guidelines, evaporator tube samples most often are not collected and analyzed, either to monitor internal deposition or as an integral part of the chemical cleaning planning process. Failure to collect and analyze evaporator tube samples before the cleaning can result in a vast underestimation of solvent requirements and an unsuccessful cleaning effort that could leave solvent saturated deposits in the HRSG tubes. This can occur despite a very conservative cleaning plan.
- Find and Fix Leaky Valves: Some HRSG units have rather severe valve leakage problems. In addition to direct solvent leakage through leaking drain valves, leaky valves in the steam system result in solvent being drawn into other areas of the steam/water cycle and can complicate efforts to keep the superheaters and turbine properly isolated during chemical cleanings. Valves which are known to leak should be replaced before attempting a chemical cleaning.

2.7 Case Study 6: Hydrochloric Acid Cleaning of Evaporator Followed by Ammoniated Citric Acid Cleaning of Superheater and Evaporator

Although the need for multiple stage cleanings was considered possible, the specific combination of a mineral acid cleaning followed by an ammoniated citric acid cleaning was not covered in the chemical cleaning guidelines for HRSG units.⁽¹⁾ The basic approach followed in this case study of using a mineral acid for the evaporator followed by an organic solvent to clean the superheater

is sound and could be adapted for cleaning other HRSG units. However, it is cautioned that many aspects of the cleaning approach applied and presented in this case study would require improvement before it could be effectively applied to other HRSG units.

2.7.1 HRSG Design

The HRSG unit in this case study consisted of a single pressure, two-drum evaporator (similar to the HRSG in the previous case study) with an upper steam drum and a lower mud drum. Initial operating pressure was 425 psig (~2.9 MPa), but the design and future operating pressure is expected to be 1025 psig (7.1 MPa). The superheated steam temperature was only 725°F (385°C). The unit had duct burners. The superheaters were T22 steel (low chromium/ molybdenum alloy).

2.7.2 Operational History and Reason for Cleaning

The unit operated for about two years before the operational cleaning was performed. During a customary annual inspection of the evaporator circuit drums, facility personnel found two tubes plugged with deposit in the bends at the lower drum. The chemical treatment program involved the application of a carboxylic acid based dispersant to the steam drum for scale control. The exact type of feedwater treatment was not reported but the chemical vendor supplying normally supplies a blend of several amines for units in which dispersant treatments are applied to the evaporator section. The types of deposits present in the evaporators (see Section 2.7.3) were indicative of deficient water treatment. Specifically, it was known that a significant amount of untreated (neither softened nor demineralized) water had entered the steam/water cycle. Also, carryover to the superheater was indicated to have occurred.

2.7.3 Evaluating Deposits and Cleaning Requirements

The chemical treatment vendor reported that the mud drum deposit samples contained calcium oxide (23%), pyrophosphate (19%), silica (18%), magnesium oxide (16%), sodium oxide (11%), loss on ignition (9%), sulfur oxide (5% as SO₃), hematite (4%), alumina (1%), manganese oxide (1%), and carbonate (<1%). X-ray diffraction analysis (XRD) detected crystalline compounds which included hydroxyapatite, magnesium silicate (Mg₃Si₂O₅[OH]₄), magnetite, and hematite.

The steam drum deposit sample was similar except that the proportion of silica was higher. Assessments by the chemical treatment vendor analizing the steam drum sample indicated that the deposit consisted of hydroxyapatite (40%), magnesium silicate (18%), silica (13%), magnesium phosphate (10%), magnetite (5%), sodium silicate (3%), magnesium sulfate (2%), alumina, and manganese dioxide. The precleaning deposit weight was 41 g/ft² (~44 mg/cm²); however, this determination was not made until after completion of the cleaning.

The large proportions of hardness and silicates present in the deposit samples suggested that an inhibited hydrochloric acid (HCl) cleaning with ammonium bifluoride addition was the most

appropriate solvent for removing deposits from the evaporator. No tube samples were collected to determine deposit weight and composition or to evaluate cleaning solvent performance in the laboratory before the cleaning. Also, no external tube sample (to evaluate the effectiveness of the solvent applied to remove heavy localized deposits) was installed for use in monitoring the progress of the cleaning process. The acid solvent formulation selected to clean the evaporator consisted of 6.5% hydrochloric acid, 0.2% common inhibitor, and 0.5% ammonium bifluoride.

While the solvent selection was based primarily on deposit composition, a side benefit of using a strong hydrochloric acid solvent is that circulation would not be required for the initial cleaning stage – provided the solvent is properly blend filled into the HRSG.

Carryover of boiler water salts into the superheater circuits of the HRSG had occurred during operation. Cleaning of the superheaters with a mild solvent was requested to reduce the inventory of foreign matter in the superheaters.

The solvent selected for the superheater cleaning was ammoniated citric acid. Since most of the hardness contamination should have precipitated in the evaporators, it was expected that the deposited materials in the superheaters would have been mainly water-soluble salts and corrosion products with a minor amount of hardness compounds. Therefore, an organic solvent was considered to be of some benefit. Also, the use of organic solvents avoided any potential concern that the hydrochloric acid and associated acid-laden sludges would not be adequately removed from the superheater during subsequent chemical cleaning rinses.

2.7.4 Cleaning System Design

Connections for the cleaning process included the superheater outlet line (via safety valve) and the economizer and mud drum drains. A 6 inch x 6 inch (15.2 x 15.2 cm) pump was provided by the chemical cleaning contractor. However, the fill-and-drain and circulation flow rates were reportedly limited by the available line sizes. Sufficient information could not be located to reconstruct an accurate cleaning system diagram. In the planning documentation, there was no mention of the installation of orifices in the downcomers to induce flow down the evaporator tubes. Further no hydraulic evaluation appeared to have been performed to ensure adequate solvent distribution.

Before the cleaning, two days were spent replacing failed and damaged tubes in the superheater and generation bank (evaporator). Steam drum internals had been removed to install the tubes, and the cleaning was performed before reinstallation of the steam drum internals. This sequence was selected to facilitate flushing and inspection of the tubes following the cleaning.

2.7.5 Chemical Cleaning Procedure and Results

Unfortunately, some of the required items included in the original cleaning specification were not provided by the cleaning contractor; these included the ammonium bifluoride for the cleaning solvent, an external heat exchanger, apparatus used for performing a solvent inhibitor

test, radios, and proper personal protective equipment (no goggles or respirators) for contractor personnel. Only one of the two flow meters required by the specification was operational during the cleaning, and no spare flow meter was provided. While the service contractor supervisory personnel were experienced, the reported lack of experience by operators supplied by the contractor was indicated to have contributed to errors and delays in the cleaning process.

During the preheat stage of the cleaning, the HRSG was packed with water. This water was circulated from the evaporator lower header through an external steam sparger and into the superheater outlet – and possibly the economizer inlet. An oil sheen was noted in the steam drum sample during this preheat circulation period. Cleaning personnel attributed this sheen to the oil lubrication pump used for the hydrostatic test conducted before starting the cleaning. However, it also could have been a result of the tube rolling operations performed before the start of the cleaning. Depending on the percentage of tubes replaced and the extent of oil contamination, performing an alkaline detergent cleaning could very well have been desirable before initiating the acid cleaning.

Once the preheat stage temperature reached 180°F (82°C), the evaporator was drained down to provide sufficient room for the premixed chemicals. The superheater was isolated and the circulation path changed. The exact circulation path was not available. However, it was indicated that the only connections were to the bottom of the evaporator and to the economizer. Therefore, it is expected that the cleaning system circulated from the bottom of the evaporator and discharged to the economizer inlet. While circulating the water, the concentrated inhibited acid was blended into the evaporator/economizer circuit. Sufficient chemical was to have been applied to obtain 6.5% hydrochloric acid and 0.2% of a common commercial inhibitor (the specified ammonium bifluoride was not provided).

The first sample from the evaporator drum contained 4.5% acid and 0.26% iron. The steam drum temperature was 150°F (~66°C). Solvent was circulated intermittently but available records do not indicate actual frequency and duration of circulation. Solvent samples were collected hourly during the hydrochloric acid soak period (approximately five hours). Figure 2-12 shows the acid and iron data for the evaporator cleaning. The significant drop (from 6.5% to 4.5%) in acid concentration following the initial fill was indicative of a substantial amount of hardness deposit removal by the solvent. While the last two iron concentration readings, collected 30 minutes apart were the same, determination of stable readings over a longer period is needed to provide a more reliable indication of deposit removal in all areas of the system. Also, for operational cleanings with HCl, a total contact time of at least six hours is needed. The iron level increased and the acid strength decreased slightly in the composite drain sample (last reading shown in Figure 2-12). Differences in results between the last circulated solvent sample of the iron removal stage and the composite drain sample could be an indication that the data trend determined by analysis of the drum and circulating solvent samples collected during cleaning was not entirely representative of all sections of the HRSG contacted by the solvent.

Mineral acids are usually considered for use when achieving adequate circulation with organic solvents is known to be a problem. As such, the greatest benefit of this solvent is obtained by performing a blend fill of the HRSG to ensure that areas with poor circulation also will be

exposed to solvent for the full contact period. A blend fill with inhibited hydrochloric acid was included in the initial specification. In the absence of any known errors in collection of the composite drain sample, it seems likely that solvent addition for this cleaning was not performed in the intended manner and that subsequent circulation did not result in thorough mixing and distribution of the solvent throughout the system.

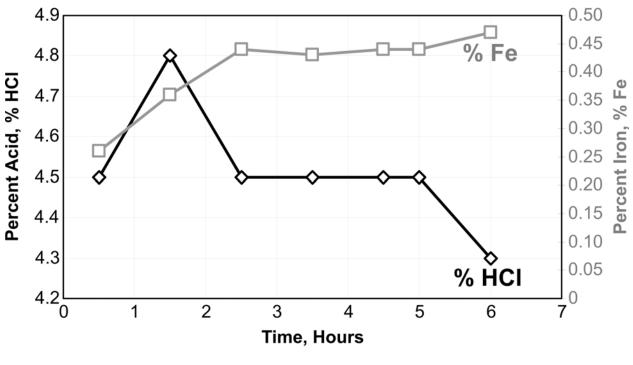


Figure 2-12 Case Study 6, Hydrochloric Acid Stage Chemistry Data

The evaporator and economizer were filled and drained with rinse water twice before proceeding with the ammoniated citric acid cleaning. To reduce the risks associated with residual hydrochloric acid in sludges or nondrainable areas, application of a soda ash (sodium carbonate) neutralization solution is normally advised before proceeding to the passivation stage. (Any residual acid and sludge piles present as a consequence of the rinsing approach taken could have had effects on the chemistry during subsequent phases of the cleaning including the final drain.) Use of soda ash with HCl is particularly useful because gas (carbon dioxide) is generated from the neutralization reaction, which can facilitate better neutralization solution distribution within sludge piles and low-flow areas.

Despite the lack of a suitable neutralization stage, it was indicated that the rinse water pH values were over 5.0, although such a pH value following rinsing is rather unlikely with only two high purity water rinses unless rinse water with some reserve alkalinity was used in lieu of demineralized water. Also, it is possible that the pH reading was higher than the actual pH due to the use of pH paper (some types of pH paper will provide erroneous readings in very dilute acid solutions). Available records give no evidence that a suitable pH meter was available for use during the cleaning.

After completion of the two rinses, the system was completely refilled with treated (presumably demineralized) water and the preheat circulation route for the superheater, economizer, and evaporator was reestablished. As the system was heating up, chemicals were blended in separately in the following sequence.

- Inhibitor.
- Citric Acid.
- Ammonia.

Following completion of the inhibited ammonium citrate injection, the system pH was 4.0, the solvent temperature was $135^{\circ}F(57^{\circ}C)$, and the circulation rate was $185 \text{ gpm}(42 \text{ m}^3/\text{hour})$. Temperatures were increased to $147^{\circ}F(64^{\circ}C)$ over a period of about three hours. Solvent temperatures (< $150^{\circ}F$, < $67^{\circ}C$) and contact times (less than four hours) were well below the levels normally used for iron oxide removal in operational cleanings employing this solvent.

As shown in Figure 2-13, insufficient iron testing was performed to obtain a meaningful concentration plateau. Only two similar iron concentrations, determined after approximately 2.5 hours of total contact time, were used to indicate that stable chemistry conditions been obtained. However, once the two similar readings were obtained, the iron oxide removal stage was considered complete and subsequently terminated. This termination was very likely premature. At least three consecutive similar readings collected with acceptable process conditions are needed to indicate a stable concentration plateau and longer contact times (3-12 hours) usually are required to ensure cleaning completion with ammoniated citric acid.

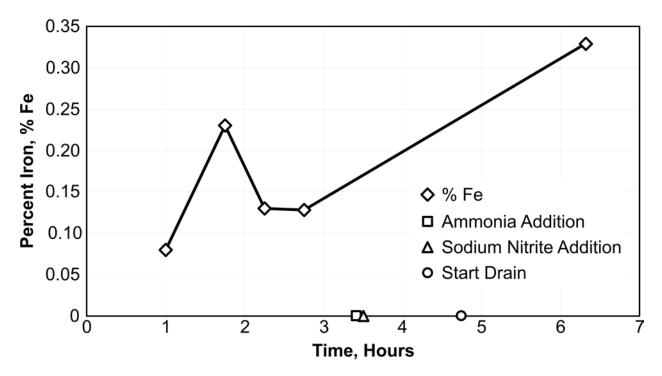


Figure 2-13 Case Study 6: Ammoniated Citric Acid Cleaning Iron Concentration Data

In preparation for the passivation stage, additional ammonia was added to raise the pH to about 9.0. Five minutes after completion of the ammonia injection and after having checked the pH (apparently at one location), sodium nitrite was added. For HRSG units, it is normally necessary to circulate the solvent and check the pH in many locations to ensure proper ammonia distribution prior to oxidant injection. If sodium nitrite had contacted acidic sludges (from hydrochloric acid stage) or slightly acidic ammoniated citric acid, then a mixture of nitrogen dioxide and nitric oxide gases could have evolved. Generally, gases formed in the system must be vented to prevent gas binding and maintain circulation. Nitrogen gases formed through acidification of sodium nitrite are noxious and would need to be vented away from personnel. Also, oxidizing acid solutions can be very corrosive.

As indicated in Figure 2-13, the iron concentration determined in the ammoniated citric acid solvent more than doubled between the end of the iron oxide removal stage and collection of the composite drain sample following the end of the passivation stage. The composite drain sample results suggest the citric acid stage removed 0.33% iron with a final pH of 4.0; this is well below the value of pH 9.0 indicated following ammonia addition preceding addition of the oxidant. This iron concentration well exceeds all iron readings reported during the solvent circulation period.

The change in iron data and the final reported pH suggest that the steps taken to adjust the pH prior to sodium nitrite addition were deficient. If the pH adjustment was suitable, the possibility exists that it was later depressed due to HCl from the first stage of the cleaning that were retained in sludge piles or system deadlegs. In the absence of these effects, the data support the view that the ammoniated citric acid stage was terminated prematurely.

The operating water volume of the HRSG was 4330 gallons (~16 m³), not including the superheater. The evaporator/ economizer system cleaning was assumed to be 4500 gallons (~17 m³) for the acid stage, and the cleaning with the superheater was assumed (at the time) to be 9000 gallons. If these volume estimates were correct, the total amount of magnetite removed was 243 lbs (110 kg) for the hydrochloric acid stage and 342 lbs as Fe_3O_4 (155 kg) for the citric acid stage based on the 4500-gallon (~17 m³) and 9000-gallon volumes (34 m³), respectively. However, the HRSG design information indicated that the volume of a completely full HRSG was only 5697 gallons (~22 m³), which usually includes the superheater. Using 5700 gallons (~22 m³) for the citric acid cleaning results in an estimated iron oxide removal of 207 lbs Fe_3O_4 (94 kg) for the monoammonium citrate stage. The specified citric acid dose (1100 lbs, 499 kg) corresponded to only ~2.3% citric acid based on 5700 gallons (22 m³).

No external tube sample was used during the cleaning to evaluate cleaning effectiveness and tube samples were not collected after the cleaning to determine if any deposit material remained. It is certainly possible that the cleaning was not successful based on the omission of ammonium bifluoride to remove the silica-rich scale from the evaporator. Also, conditions during the short duration ammoniated citrate cleaning were probably insufficient to have any meaningful success in effectively removing operational deposits from the superheater tubes.

Cool, untreated water from the fire protection system was used for final rinsing the HRSG after cleaning and this activity (as well as the various possible deficient aspects of the final passivation stage mentioned earlier) may have contributed to observations of surface rusting noted during a postcleaning inspection.

2.7.6 Lessons Learned

- Hydraulic Evaluation: Perform a hydraulic evaluation before developing a bid specification so that all bidders will be required to provide adequate solvent distribution and movement.
- Oil Contamination: If it is possible that sources of oil may be introduced during precleaning activities (tube rolling, oil in hydrostatic test pumps, etc.), consider performing an initial alkaline detergent cleaning. Since a large proportion of the known HRSG operational cleanings has involved partial tube replacement, this may be applicable to a significant number of facilities.
- Cleaning Sequences Using Hydrochloric Acid: The bulk of deposits can be removed from evaporators using inhibited hydrochloric acid. Provided it is verified that all acid is thoroughly drained and flushed from the system, this can be followed by organic based solvent such as ammoniated citric acid to either finish the cleaning and/or to clean contiguous areas such as superheaters for which hydrochloric acid would not normally be used.
- Hydrochloric Acid Neutralization: Sludge removal and application of soda ash should be considered after all hydrochloric acid stages and before performing a passivation stage involving oxidants.
- Blend Fill Solvents. If the cleaning system design cannot ensure uniform solvent distribution, then perform a blend fill with the cleaning solvent and subsequent neutralization and passivation stages. To reap the benefits of hydrochloric acid, the evaporator should be completely drained and the acid applied by controlled blend filling. After rinsing, a neutralization stage should be applied in a similar manner.
- Cleaning Specification Compliance: Contractors do not always comply with the cleaning specification, even when no exceptions are included in their proposal to perform the work. Compliance with the specification should be evaluated and documented. Failure to comply with the specification may require other changes during the cleaning process to obtain an effective cleaning. Also, this documentation can be used to obtain refunds on the cost of the cleaning or as the basis for selecting cleaning contractors for future cleanings.
- Contact Time and Temperature: Even if iron oxide removal is expected to be low, allow for minimum contact times and temperatures as provided in the EPRI cleaning guidelines. (1) Longer contact times may be required for cleanings performed at lower than optimum temperatures. Also, at least three similar consecutive readings are needed over a pre-established minimum contact period to indicate a plateau in the iron oxide removal phase.
- Ammonia Distribution for Passivation: For ammoniated citric acid cleanings, allow at least one hour following final ammonia addition to test all possible areas of the HRSG for proper pH values (>9) before application of the oxidant and periodically check the pH during

circulation. In this case study, the possibility exists that corrosion may have occurred during an improperly executed ammoniated citric acid passivation stage.

2.8 Case Study 7: Dual-Pressure HRSG, Acid Phosphate Corrosion, Sodium Citrate Cleaning

2.8.1 HRSG Design

The HRSG units are dual-pressure units with HP and LP drum pressures of 1550 psig (10.7 MPa) and 250 psig (1.7 MPa), respectively. The unit does not have duct burners. Two HRSG units supply steam to one steam turbine (two-on-one arrangement).

2.8.2 Operational History and Reason for Cleaning

After about 3.5 years of commercial operation, leaking tubes were detected in both HRSG units. Four months before the tube samples were collected for cleaning assessment, HRSG-A had operated for about 26,000 hours with 300 startups and HRSG-B had operated for about 28,000 hours with 365 startups.

2.8.3 Evaluating Deposits and Cleaning Requirements

Leaks were found mainly in the hottest (first three) rows of the HP evaporator tubes. For HRSG-B, tubes were found to have very localized corrosion on the bottom portions of HP evaporator inlet tube elbows (first three rows of inlet tubes). Bottom sections of the HRSG-B HP evaporator tubes were replaced with straight (no fins) tubes, but soon thereafter it was realized that the problem was more extensive.

One month after the initial failures, borescopic inspections and tube sampling were performed. Following are the key findings from these evaluations.

- HRSG-A HP Evaporator Deposit Locations: With the exception of some accumulations of sludge in the three outlet rows (i.e., coolest section based on gas-side flow), borescopic inspection revealed that evaporator tubes were in generally good condition.
- HRSG-B LP Evaporator Deposit Locations: All tubes had nonuniform accumulations of moderate corrosion products as viewed from the lower mud drum and upper collector drum.
- HRSG-B HP Evaporator Deposit Locations: The heaviest corrosion product accumulations were in the cooler tubes (center and outlet ends of the evaporator tube bank). Borescopic inspection from the steam drum indicated that HRSG-B HP evaporator tubes had greater deposits on the outlet (coolest) rows than on the inlet (hottest) or interior rows.
- HP Evaporator Tube Deposit Weight: Typical deposit weights were generally 7-8 g/ft² (7.5-8.6 mg/cm²) as determined by glass bead-blasting. However, deposit weights approached

 300 g/ft^2 (322 mg/cm^2) in localized areas due to in situ corrosion (underdeposit corrosion. Appearing as gouges).

- HP Evaporator Tube Deposit Composition: Copper plating was noted on metal surfaces. Deposits away from the gouges consisted primarily of iron (81%), copper (8%), manganese (4%), silicon (2%), and lesser amounts of other miscellaneous oxides. In the gouged regions, the deposits consisted primarily of iron (40-66%), copper (2-25%), phosphorus (1-26%), sodium (0-23%), and manganese (4-9%), with lesser amounts of silicon (0-2%) and other miscellaneous oxides. Maricite was found beneath deposits in the gouged region, which confirmed acid phosphate corrosion as an active corrosion damage mechanism. The loss on ignition of deposits was 1-2%, where tested.
- HP Evaporator Tube Condition: Severe deposits and underdeposit corrosion affected many tubes. Acid phosphate corrosion was indicated to be the responsible damage mechanism. The front halves of the HP evaporators were replaced one year after the initial tube failures.

2.8.4 Chemical Cleaning Procedure and Results

About one year after the initial tube failures, tubes were replaced and a sodium citrate cleaning was performed. Based on available file records it appeared that the HRSG-A HP and LP evaporator sections were cleaned simultaneously. Then, the HRSG-B HP evaporator section was cleaned alone. A comprehensive videoscopic inspection after the cleanings indicated that deposits remained at many locations. Some of the corroded areas (which had not been replaced) had been cleaned and others had not. Overall, deposit removal in the HRSG-B HP evaporator was more effective than for HRSG-A HP and LP evaporators. This difference was attributed partly to an attempt to clean the HRSG-A HP and LP sections simultaneously, which resulted in lower flow rates to individual sections. While often adequate for preoperational cleanings, the temperature was low (160-180°F, ~71-82°C) and the contact time was short (four to six hours) for an operational cleaning. Higher temperatures (180-200°F, ~82-93°C) and longer contact times were planned for future operational cleanings (minimum of 12 hours).

No external tube specimen was available for inspection during the cleaning process to confirm cleaning effectiveness. In some cases, a chemistry plateau in the bulk solvent indicates only cessation of deposit removal from most surfaces. However, when severe localized deposits are present, an external tube sample is the preferred way to effectively confirm that the cleaning is successful. Soft, nonadherent deposits were present in the bottoms of sloped sections of the evaporator tubes following the cleaning. The level of passivation achieved ranged from very satisfactory to marginal.

To reduce the potential for additional acid phosphate corrosion, chemistry control was changed to a program more consistent with EPRI guidelines. The primary changes for boiler water chemistry involved reducing the phosphate concentration and extending the upper pH range to allow for up to 1 ppm of free caustic in the boiler water. These measures reduced both phosphate hideout and the actions that fueled the acid phosphate mechanism (i.e., the operators no longer tried to maintain congruent phosphate treatment).

2.8.5 Lessons Learned

- Deposit Location: In some HRSG designs such as the one in this case study, heavy deposits can accumulate in the coolest rows of evaporator tubes and not lead to tube failures in this region. Therefore, sampling only those tubes from the front, hottest rows of the evaporator may result in underestimating the extent of deposition and associated cleaning requirements.
- Contact Times and Temperatures: Low temperatures (160-180°F, ~71-82°C) and contact times (four to six hours) used for some preoperational cleanings with citrate solutions were found to be inadequate for operational cleanings (after 3.5 years of service) in a HRSG with severe and localized solids accumulations resulting from underdeposit corrosion damage.

2.9 Case Study 8: Dual-Pressure HRSG, Chelant Cleaning

2.9.1 HRSG Design

In this case study, four dual-pressure HRSG units with HP/LP drum pressures of 1020 psig (7.0 MPa) and 207 psig (1.4 MPa) were cleaned after a brief period of operation.

2.9.2 Operational History and Deposit Evaluation

After six months of periodic commercial operation, evaporator tubes failed while the unit was believed to be in a dry nitrogen layup. The HRSG units were not completely drained, and the expansion of water during freezing resulted in tube ruptures. Further investigation indicated that the units could not be effectively drained due to a combination of unusually small drain lines (0.5 inch or 1.27 cm inner diameter elbows), excessive pre-service corrosion, a lack of preoperational cleaning, and plugging of the drain lines by iron oxides during service. Videoscopic inspection confirmed that a cleaning was required. The units were chemically cleaned two months after the freeze failures were detected (which followed eight months of intermittent operation). The deposits to be removed were primarily iron oxides. While tubes were inspected prior to the cleaning, any information that may have existed on tube sampling and deposit weight data could not be located during preparation of this document.

2.9.3 Chemical Cleaning Design

The HP and LP sections were cleaned in parallel for each of the four HRSG cleanings. The steam drums were completely filled (i.e., packed system), and external circulation and heating were used to provide the required solvent movement and temperatures for the chelant cleaning. Adequate flow monitoring was not available from the cleaning contractor, but the size of the pump used was estimated to have had the capability of displacing one system volume in about seven minutes. While the authors were able to locate the log of operations, a drawing of the system could not be located. Sufficient time had elapsed since performance of the cleaning that it was not possible to exactly recreate the system design from memory.

2.9.4 Cleaning Procedure and Results

Chemical cleanings employed diammonium EDTA and were judged to be effective based on videoscopic inspections made before and after the cleanings. The total amount of iron oxide removed was rather low (0.27-0.36% Fe). Typical operational cleanings remove 0.5-1.0% iron. This indicated that the deposits were rather localized. The contact time was set at 20 hours at the target temperature. For the four HRSG cleanings, solvent temperatures (minimum 148-160°F [64.4-71.1°C], typical 165-170°F [73.9-76.7°C], and maximum 179°F [81.7°C]) were relatively low for an operational cleaning, but were in line with standard practice for preoperational cleanings. Temperature was limited due to the use of hoses in the cleaning circuit. This also indicated that the deposit materials were more likely pre-service related, as the temperatures may have been inadequate for typical operationally formed deposits. For each cleaning, the HRSG units were preheated, hot water was drained to a clean, portable waste tank, and the units then blend filled with EDTA solution to ensure that the solvent was properly distributed. Therefore, the chemical was in contact with the system for an additional one to eight hours during the reheat step (up to the desired temperature for the cleaning). Even though the total iron removal was rather low, formic acid needed to be added periodically on all four HRSG cleanings to lower the pH to about 5.5 (similar values were obtained by the contractor and station laboratory).

2.9.4.1 Passivation

During cool down of the packed system (in preparation for the passivation stage), the liquid contracted and created a vacuum. Some of the hoses exposed to the vacuum collapsed. Pressure gauges not designed for a vacuum also may have been damaged. Pressure was reestablished through liquid (aqua ammonia) injection.

For all four HRSG cleanings, ammonia was added to the HRSG while circulating. The HRSG was drained under nitrogen and oxidized with sodium nitrite and then air in a portable storage tank, and the oxidized passivation solution reinjected back into the HRSG. Due to high EDTA and low iron concentrations in the solvent, iron levels rose during the first three passivation stages. No change in iron concentration was noted for the last cleaning. However, the level of passivation achieved was satisfactory for all four cleanings based on postcleaning videoscopic inspections.

2.9.5 Lessons Learned

- Contact Time and Temperature: For a HRSG with deposits exposed to only eight months of operation, longer contact times (20 hours) were able to compensate for the reduced cleaning performance at low temperatures (~160-180°F, ~71-82°C) with diammonium EDTA solutions.
- Formic Acid Addition: In these packed systems, periodic formic acid addition was needed to maintain pH values of <5.5 (as needed for sufficiently rapid iron oxide removal).

- Blend Filling with Organic Solutions. Blend filling HRSG units with organic solvents and passivation solutions was used to compensate for nonuniform or marginal circulation rates.
- Avoid Vacuum Conditions: Just as the vents must be operated to bleed off excess gases and liquids during heating, liquid needs to be added to keep the system packed during cooling periods. Failure to maintain system pressure caused hoses to collapse and halt solvent circulation.

2.10 Other Case Studies

Discussion of Case Studies 9-12 (listed in the summary table in Section 1, Table 1-1) was not included herein because either there was insufficient information or the lessons learned were considered an unnecessary duplication of the lessons learned in the other case studies. A pervasive lesson learned in all of the operational cleanings of HRSG units in the database is the need to perform a hydraulic evaluation to determine the circulation requirements for organic solvents and sometimes the need to consider solvents which do not require such extensive circulation.

2.11 References

- 1. *Heat Recovery Steam Generator (HRSG) Chemical Cleaning Guidelines*, EPRI, Palo Alto, CA: 2003. 1004499.
- 2. Interim Cycle Chemistry Guidelines for Combined Cycle Heat Recovery Steam Generators (*HRSGs*), EPRI, Palo Alto, CA: 1998. TR-110051.
- 3. Cycle Chemistry Guidelines for Combined Cycle Heat Recovery Steam Generators (HRSGs), EPRI, Palo Alto, CA: 2006. 1010438.

3 ALTERNATIVES TO CHEMICAL CLEANING

3.1 Introduction

Because of some of the problems associated with effectively chemically cleaning HRSG units, some attention has been directed to chemical cleaning alternatives. First and foremost would be the prevention of deposit formation through an effective steam/water cycle chemical treatment program, based on the latest cycle chemistry guidelines. ⁽¹⁾ However, once deposits have developed and/or tube failures have occurred, the following options have been considered as an interim measure to defer or avoid chemical cleaning of evaporator tubes.

- Tube Replacement.
- Hydrojetting Tube Internal Surfaces.
- Avoid Use of Duct Burners.
- Better Chemistry Control.

Partial tube replacement is required whenever the tubes have failed or experienced significant underdeposit corrosion. Once a tube has significant localized corrosion product accumulations, it is generally not possible to stop the progression of additional underdeposit corrosion unless the deposits are removed. The process of removing deposits during a cleaning sometimes can lead to further localized corrosion, resulting in solvent leaks during the cleaning or additional failures following the cleaning. (Failures at such locations are likely to be imminent, even if cleaning is not performed.) Tubes which have experienced significant localized corrosion are typically more prone to continued deposition after they have been properly cleaned due to the flow disruption effects of prior damage sites. Therefore, sometimes it is preferable to replace the tubes rather than chemically cleaning them. In one example presented herein, the need to replace the tubes was obvious. However, in other cases, the extent of tube replacement required or desired is not as well defined. It could involve such considerations as the code required minimum wall thickness, surface roughness effect on circulation and future deposition, the cost of chemical cleaning versus that of tube replacement, outage time required, availability of materials, potential for future chemistry upsets, and/or desired future reliability of the unit. This is a complex decision that requires detailed assessment on a case by case basis.

Mechanical deposit removal by means of high pressure jetting or hydrojetting of tubes has been effectively performed for a number of HRSG units where the tubes are rolled into accessible upper and lower drums. This arrangement greatly facilitates the use of hydrojetting for routine maintenance to control deposit accumulations. This design was more common for smaller and

simpler HRSG units used mainly in cogeneration applications. There also was one instance (Case Study 16) where the upper evaporator headers were cut open for videoscopic inspection and hydrojetting was subsequently performed to remove localized accumulations of thick scale. Where feasible, hydrojetting also can be used as a preliminary step to clear obstructed tubes before chemical cleaning and as a measure to defer (perhaps indefinitely in low pressure units) chemical cleaning. This section provides some information on a few facilities which are known to have used hydrojetting to mechanically clean tubes.

Operation of duct burners, provided on some HRSGs, increases tube metal temperatures during operation, which can lead to increased underdeposit corrosion and phosphate hideout on waterside tube surfaces. For some HRSG units which have experienced tube failures, partial tube replacement was accomplished during one outage and then chemical cleaning was completed in a separate outage several months later. During this interim period, the duct burners were not placed in operation so as to minimize the potential for tube failures. Some HRSG units which experience fairly limited operation could perhaps consider longer term avoidance of duct burner usage to minimize underdeposit corrosion.

While the benefits of a well designed, well managed chemistry program are greatest if maintained from the start of commercial operation, it is never too late to improve chemistry control in operating HRSG units. Improvements to the chemistry control program can have immediate effects on corrosion product transport to the evaporator and underdeposit corrosion reactions in the evaporators. For example, in the case of units experiencing phosphate hideout and/or acid phosphate corrosion, exclusive use of trisodium phosphate (and caustic as needed for pH control) prevents acid phosphate corrosion. Altering the cycle chemistry treatment program to reduce the transport of corrosion products and corrodents to the HRSG units will decrease the rate of additional deposit growth in the evaporator sections. However, these chemistry changes do not obviate the need to eventually remove previously formed waterside deposits in order to completely eliminate the potential for underdeposit corrosion of evaporator tubes.

The following case studies present the experiences of facilities with HRSG units which have either performed hydrojetting cleanings of evaporator tubes or opted for tube replacement in lieu of performing operational chemical cleanings. In addition, some of the case study facilities have evaluated limiting the use of duct burners and improving their chemistry control program to reduce the rates of deposition and corrosion.

3.2 Case Study 13: Tube Replacement

An incomplete account of relevant information was available for this case study. The unit was a 2100 psig (14.5 MPa) HRSG which experienced evaporator tube failures after three months of service. As indicated in Figure 3-1, severe underdeposit corrosion was evident.

The deposit was about 0.25 inch (~0.63 cm) thick, and the deposit weight was determined to be 822.6 g/ft² (~885 mg/cm²) by a mechanical method of deposit removal (slightly different than Method A of ASTM D-3483). Deposit weight removal methods are discussed in Reference 2. ⁽²⁾

The scale consisted primarily of the base metal oxide (\sim 99% iron oxide and \sim 1% manganese oxide). A full investigation into the mechanisms and root causes of the corrosion and deposit accumulations was not performed.

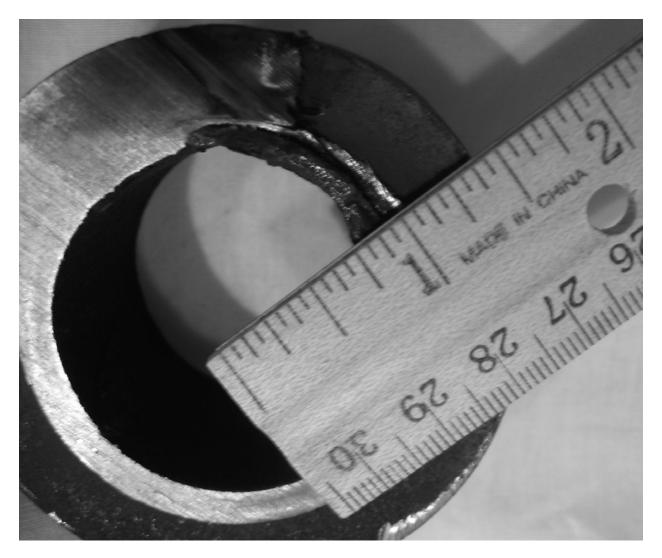


Figure 3-1 Case Study 13 Tube Sample Source: Courtesy of George Bodman, Inc.

The tube wall measurement was determined to be well below the required wall thickness for continued operation. Perhaps as a demonstration of the futility of chemical cleaning, a laboratory tube cleaning test with four sequential hydrochloric acid stages resulted in through-wall perforations in the tube sample with about 16 g/ft² (~17 mg/cm²) of deposition remaining at other locations.

3.3 Case Study 14: Hydrojetting Single Pressure, Two-Drum HRSG

3.3.1 HRSG Design

This facility employed two dual-pressure HRSG units with HP and IP drums operating at pressures of 900 psig (6.2 MPa) and 280 psig (1.9 MPa), respectively. The units used both natural gas duct burners and hydrogen gas duct burners.

3.3.2 Operating History and Deposit Evaluation

This unit had a history of corrosion fatigue cracking in the upstream economizer sections before problems in the evaporator tubes were realized. Since this information was considered relevant in characterizing the operational history of the units, it is included herein.

Periodic LP economizer tube failures occurred due to corrosion fatigue cracking and failure assessment revealed signs of pitting and intergranular corrosion were noted. These failures were first detected after four years of operation and continued for an additional nine years. Maximum pit depths were up to 22 mils (0.56 mm). Scanning Electron Microscopy/Energy Dispersive X-ray Spectroscopy (SEM/EDXS) deposit analyses detected mainly iron (94-99%) and nickel (0-4%) with only traces (<1%) of other metals (chromium, titanium, copper, aluminum), phosphorus, silicon, and sulfur.

After 13 years of operation, HRSG-B evaporator tubes failed and contained severe waterside deposits (almost plugged) and chip scale in the bottom elbows. A heavy, bright hematite color was apparent on the surface of the deposits. Heavy black deposits also were visible. These failures occurred in the hottest row of evaporator tubes, about midway across the gas pass. The tube failures were experienced just after the bend out of the mud drum (lower header). Minor bulging was visible in the tubes. Extensive oxidation of the fins was apparent; they were brittle and easily knocked off. Waterside deposit composition by X-ray Fluorescence (XRF) was mainly iron (41-45%), copper (38-54%), phosphorus (2-7%), magnesium (0-4%), calcium (1-4%), loss on ignition (1%), and nickel (1%). The tubes had thinned to 32-52 mils (0.8-1.3 mm). No pits were noted. Evidently, the tubes had become plugged with deposits, causing them to overheat and fail. X-ray Diffraction results indicated major amounts of copper, magnetite and hematite and minor amounts of cuprite (Cu₂O), magnesioferrite (MgFe₂O₄), and calcium hydrogen phosphate hydroxide (Ca₉HPO₄(PO₄)₅OH).

An evaluation of the system found that the sources of copper were the 90/10 Cu/Ni steam surface condenser, the bronze impellers on the hotwell pumps, and the copper-based catalyst in the process condensate. Sodium leakage from sodium-cycle condensate polishers and problems with the makeup demineralizers (cation resin in anion units) introduced caustic to the evaporator water. The elevated sodium concentration in the feedwater most likely required the addition of acidic phosphates to control boiler water pH in the chemical treatment vendor's recommended pH/phosphate control range. The source(s) of hardness was not reported in their evaluation.

The feedwater treatment program consisted of an organic reducing agent (hydroquinone) and an organic amine blend. The units were operated with 2% blowdown (50 cycles of concentration).

3.3.3 Mechanical Deposit Removal by Hydrojetting

Since tubes were plugged with chip scale, mechanical cleaning was required before chemical cleaning could be considered. Since the tubes were already being hydrojetted, it made sense to extend the operation to clean all accessible evaporator tubes to the extent possible. With mechanically cleaned tubes and improved chemistry control, there was the expectation that chemical cleaning could be safely avoided in this low pressure unit.

3.4 Case Study 15: Hydrojetting Single Pressure, Two-Drum HRSG

3.4.1 HRSG Design

This industrial facility has a large number (indicated to be 16 HRSG units) of small, single pressure, low pressure (700 psig, ~4.8 MPa), low superheat (950°F, 510°C) HRSG units. The HRSG units receive waste heat from ovens at a steel mill. These units have upper and lower drums and roof tubes. At the time the information was compiled, the units were about seven years old.

3.4.2 Operating History and Deposit Evaluation

The HRSG units are essentially baseloaded with one or two maintenance outages per year. The primary purpose of the maintenance outage was to clean the gas pass. The steel mill waste gas is dirty and fouls the outer diameter (gas side) of the HRSG tubes. The HRSG units have a common feedwater system. Two deaerators receive a mixture of turbine condensate (59%), reverse osmosis (RO) permeate makeup (29%), and process condensate (12%) from the steam host. While the HRSG units provide steam to the steel mill and condensate return from the steam host, it was stated that the steam sent out is used in other areas and none is returned. The process condensate return was solely condensate from other boilers supplying the steel mill.

The makeup system consists of ion exchange softeners followed by RO units. Typically, the RO effluent conductivity and pH were about 10μ S/cm and 7.8-8.2, respectively. It was reported that the sodium leakage from the makeup system normally exceeds 1 ppm. The low pH values indicate that significant amounts of carbon dioxide or other anion(s) also are present in the RO effluent. If the predominant compound in the RO effluent is sodium bicarbonate, some carbon dioxide can be lost as it passes through the deaerator. This would result in more alkaline feedwater pH values. However, significant free caustic would not be expected until the water was concentrated in the evaporator.

Feedwater treatment for this unit involved feeding large amounts of a reducing agent. The exact amine blend (required by steam host) for steam condensate pH elevation was not specified. The steam provided to the host often had pH values below 8.5.

The facility was experiencing about 16 economizer tube failures per year during early operation due to waterside thinning of the economizer tubes (i.e., iron transport to evaporator section). The mechanism of economizer tube wall loss was inferred to be single phase flow accelerated corrosion (FAC). No additional economizer tube failures have occurred since use of the reducing agent treatment was terminated.

Following the initial plethora of economizer tube failures, evaporator tube failures were experienced. Heavy deposits, caustic gouging (primary failure mechanism), and corrosion fatigue damage were detected in the evaporator tubes. Signs of steam blanketing (steam/water stratification) also were reported in evaporator tubes. The deposits consisted primarily of iron oxide, although significant copper also was indicated to be present. While caustic gouging was the primary failure mechanism and a source of iron oxide on tube surfaces, the initial iron oxide deposition required to activate the caustic gouging mechanism was attributed to iron transport resulting from FAC damage of the economizer tubes. Process condensate from the steam host was an additional source of iron and also the copper reported in the evaporator tube deposits.

Based on failure mechanisms and the water supply information provided, a reduction in tube deposit formation rates and failures would require improvements in makeup water and steam host condensate purity. There were indications that the feedwater treatment program had been improved. Improvements included eliminating the feed of the reducing agent to prevent single phase FAC. Also, on-line conductivity and pH meters were installed on the process condensate to detect severe contamination incidents. Since installation of these analyzers process condensate was sent to the sewer at least once, this because of excessive conductivity and elevated pH.

On-line conductivity meters also have been installed to monitor the blowdown from each evaporator. This has enabled better control of specific conductivities (and free caustic levels) in the evaporators. Control ranges were reduced for both conductivity (from 125-175 μ S/cm to normally <50 μ S/cm with a maximum limit of 75 μ S/cm) and phosphate (from 10-20 ppm to 2-5 ppm as PO₄) in an effort to minimize solids and free hydroxide levels in the evaporator water. Evaporator blowdown pH values now are normally 9.5-10.0. However, due to contract limitations, the water treatment program is not expected to be able to comply with EPRI chemistry guidelines in the foreseeable future.

No further economizer tube failures have been experienced since the reducing agent feed was eliminated over one year ago. While less frequent as a result of changes in chemistry, evaporator tube failures have continued. However, the most recent failures appeared to have been caused by external surface corrosion.

3.4.3 Mechanical Deposit Removal by Hydrojetting

The facility is currently managing tube deposit accumulations and the frequency of evaporator tube failures by hydrojetting the tubes on an annual basis. The hydrojet pressure used is 5,000-10,000 psig (~34-69 MPa) for these cleanings. Figure 3-2 shows a typical evaporator tube before hydrojetting.

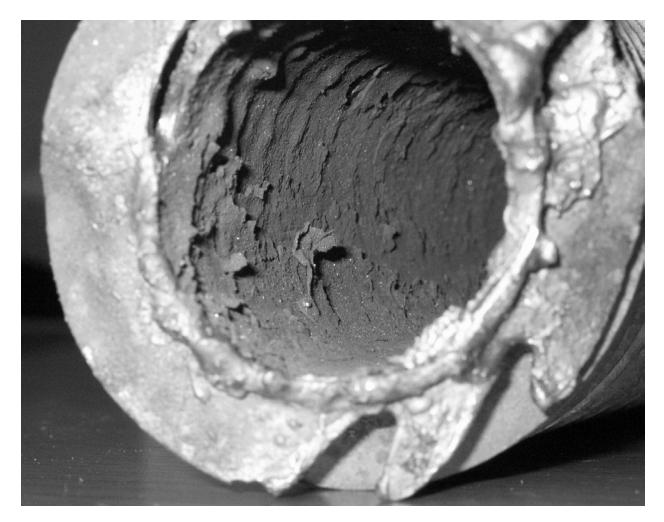


Figure 3-2 Case Study 15, Typical Evaporator Tube Before Hydrojetting Source: Courtesy of George Bodman, Inc.

3.5 Case Study 16: Hydrojetting in Lieu of Chemical Cleaning

The HRSG in this case study had a drum pressure of 650 psig (4.5 MPa) and provided steam to a small steam turbine and a steam host. The HRSG unit was cycled off for five- to eight-hour periods on a daily basis during the week and was out of service during most weekends. Economizer tube failures were experienced due to thermal fatigue and corrosion fatigue failure

mechanisms. In response to observations of high dissolved oxygen levels at unit startup, high levels of reducing agent were applied to the feedwater. Startup chemistry conditions were believed to have led to both accelerated iron transport to the HRSG unit and heavy accumulations of iron oxide deposits in some of the evaporator tubes.

Figure 3-3 presents a view of one of the evaporator tubes with excessive waterside deposits. This evaporator tube was removed from the HRSG following an evaporator tube failure. In response to the tube failure, a videoscopic inspection was performed of the evaporator tubes. This required cutting into the upper evaporator headers to run the videoscope probe down the tubes. Based on the videoscopic survey, it was determined that roughly 80% of the evaporator tubes were essentially clean and that heavy deposits were restricted to a very small number of tubes along the outside lanes of the evaporator sections. Because of the high cost of chemical cleaning, it was instead elected to use hydrojetting to remove internal deposits from tubes in the outer lanes of the evaporators. Access for hydrojetting was facilitated by cutting into the headers for the evaporators. It was reported that the thicknesses of waterside deposits in these tubes were significantly reduced by the hydrojetting. The effectiveness of mechanical removal of waterside deposits was determined visually, based on videoscopic inspections made following hydrojetting operations. No further evaporator tube failures have occurred since implementing the program of annual hydrojetting almost 10 years ago. To avoid high dissolved oxygen levels during startups, mechanical vacuum pumps were installed to maintain condenser vacuum during nightly off-load cycles of the HRSG units. This reduced condensate dissolved oxygen levels substantially, after which feed of the reducing agent was eliminated.

In some cases, such extreme deposit thicknesses may require the combination of mechanical and chemical cleaning methods to obtain reasonable cleaning effectiveness. Cleaning effectiveness can be evaluated in trials on tube samples removed from the unit or via on-site videoscopic inspection during hydrojetting operations.

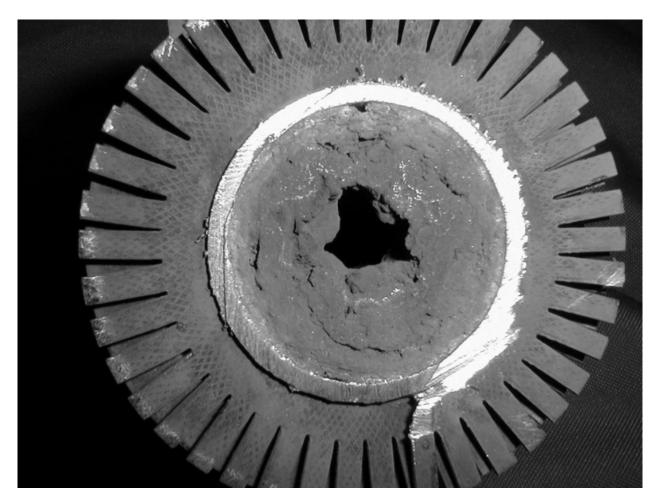


Figure 3-3 Case Study 16: Evaporator Tube before Hydrojetting

Source: Courtesy of William Strohman

3.6 References

- 1. Cycle Chemistry Guidelines for Combined Cycle Heat Recovery Steam Generators (HRSGs), EPRI, Palo Alto, CA: 2006. 1010438.
- 2. *Heat Recovery Steam Generator (HRSG) Chemical Cleaning Guidelines*, EPRI, Palo Alto, CA: 2003. 1004499.

4 PROJECT SUMMARY AND RECOMMENDATIONS

4.1 Introduction

This section provides a summary of the lessons learned through review of the 16 HRSG cleaning case studies. Many of the negative experiences reported at these facilities could have been avoided if existing EPRI guidelines for HRSG cycle chemistry ⁽¹⁾ and chemical cleaning ⁽²⁾ had been followed.

The presentation also identifies some work needed to address the unique needs of modern HRSGs and these needs ultimately need to be addressed through research and revision of the 2003 cleaning guidelines ⁽²⁾ so that the need for cleaning can be more readily established and cleaning requirements can be optimally defined and planned for.

4.2 Reasons for Cleaning

The primary reason to perform chemical cleanings of HRSG units following periods of operation has been evaporator tube failures. Once tube failures have been experienced, the availability and reliability of the unit have been irreversibly affected (without retubing). Some HRSG facilities have performed chemical cleanings before detection of tube damage in response to chemistry upsets or the detection of deposits by videoscopic inspection or tube sampling. In one case study, a tube failure involving a damage mechanism not requiring formation of heavy waterside deposits prompted a videoscopic inspection which resulted in the detection of significant deposits. For the future, a more proactive outlook on monitoring HRSG tube deposits is needed. To facilitate proactive monitoring activity, improved methods for tube examination and deposit appraisal need to be developed for use at HRSG facilities.

4.3 HRSG Deposit Evaluations

The presence of phosphate compounds beneath residual deposits left behind following an operational HRSG chemical cleaning emphasized the need for effective cleanings. Failure to obtain a tube sample before chemical cleaning resulted in substantial underestimation of the solvents required for one multistage cleaning. While tube failures are usually detected in the first few rows of evaporator tubes, greater amounts of deposits have been found in cooler rows of tubes in some cases. Therefore, nondestructive scanning methods are needed to evaluate the HRSG in order to obtain representative tube samples to assess when cleaning is required.

Videoscopic inspection was one method commonly used by the facilities for which operational cleaning has been performed to evaluate HRSG cleanliness and to locate areas of heaviest deposition. Once these areas are located, tube samples need to be collected and analyzed for deposit weight and composition analyses and tube cleaning assessments.

While the initial application of nondestructive methods presently envisioned would be to identify areas with surface deposits, it my eventually be possible to develop technology that can assess deposit thickness and collect small samples for laboratory analysis. In this way the need to collect tube samples for comprehensive laboratory assessment would be reduced though not completely eliminated as tube samples would still be needed for evaluation of suitable cleaning solvents and process conditions and to assess the condition of the tube metal.

4.4 Planning for Chemical Cleaning

Once deposit weight and composition have been determined, the single most important aspect of planning for chemical cleaning of HRSG evaporators is the performance of a hydraulic evaluation to assess the ability to attain effective distribution and circulation of the cleaning solvents and passivation solutions. This is desirable in HRSGs with simple circuitry and critical in the more complex HRSGs typically used in combined cycle power generation service. The ability to develop a suitable circulation system will dictate the types of solvents that can be effectively used and the manner in which they are applied.

4.4.1 Solvent Distribution and Circulation

For the removal of operational deposits, it has become increasingly apparent that establishing effective circulation can require massive circulation systems and significant modifications to the drain and feeder pipes of the evaporators. While the power industry has moved away from the use of inhibited hydrochloric acid for the cleaning of conventional boilers, blend filling HRSG units with inhibited hydrochloric acid (followed by soda ash neutralization) needs to be considered for the operational cleaning of some HRSG units where the circulation requirements of organic solvents cannot be met. Blend filling also has been used for operational cleanings of some HRSG units with organic solvents to ensure uniform solvent distribution where marginal external circulation can be provided. The most important lessons relating to planning for a chemical cleaning are as follows.

• Perform a hydraulic evaluation before preparing a bid specification so as to determine the requirements for an effective cleaning (e.g., to obtain at least ~1 ft/s or ~0.3 m/s fluid velocity in all tubes). However, it is not useful to state a minimum velocity in a bid specification if this velocity cannot be attained with the particular HRSG unit. The engineering work must be done to determine if the attainment of the desired minimum velocity is feasible. Results of the hydraulic evaluation provide the basis for the specification and evaluation of circulation designs in proposals submitted by bidders. Additionally, a thorough analysis of HRSG design details is suggested to insure that the information used to perform the hydraulic evaluation is accurate.

- Connections to the HRSG units can be effected through existing flanged connections, newly installed high-pressure flange connections, flanged pressure relief valves, and steam drum manway connections. (See Figure 2-2.)
- Orifice plates generally need to be installed in HP evaporator downcomers for forced (pumped) circulation through evaporator tubes. While not used in any of the case studies, an alternative circulation approach is possible based on gas-induced circulation up the downcomers and down the evaporator tubes. Orifices would not be needed with this approach; however, increased venting capacity may need to be provided.
- If 1 ft/s (0.3 m/s) fluid velocities cannot be provided, blend filling of the solvents and passivation solutions is suggested to ensure adequate distribution for operational cleanings.
- Specify dedicated flow meters for each area requiring flow monitoring. Moving strap-on flow meters is time consuming and can provide variable results.

4.4.2 Solvent Selection

The following points need to be accounted for when considering the suitability of cleaning solvents.

- If hydraulic analysis results indicate that some areas of the system to be cleaned will have little or no circulation, evaluate the use of strong mineral solvents such as hydrochloric acid for iron oxide removal.
- If hydrochloric acid is used for iron oxide removal, soda ash should be applied to help ensure effective neutralization of the acid in sludge piles.
- Designate the types and amounts of solvents to be used in the specification based on results of evaluation of deposits and/or laboratory tube cleaning testing. All materials and equipment needed for the cleaning, including the required gases (e.g., nitrogen for draining hydrochloric acid, and supplemental gaseous oxidants for ammoniated EDTA and ammoniated citric acid cleanings) should be defined in the cleaning specification.
- If proprietary solvents are to be used, a laboratory cleaning assessment should always be performed before the cleaning to demonstrate effectiveness.
- Compatibility of the cleaning solvent with the system materials of construction must be verified before the cleaning.

4.4.3 Miscellaneous Planning Considerations

Other factors in the planning process which may seem rather simplistic or mundane can greatly aid in the performance of an effective cleaning. Some of these additional suggestions are provided in the following list.

• Install troughs or use large totes to enable visual observation of liquid discharges from vent hoses. Do not use troughs on pressurized solvent or rinse drains as they will restrict drain rates or back up and overflow.

- Use computerized data collection systems to track the numerous thermocouple readings in the HRSG during the cleaning. This can be invaluable for assessing both temperature distribution and solvent circulation in the system.
- Bid specification requirements should be written to ensure that the selected cleaning contractor has extensive experience providing similar cleanings at other facilities coupled with a good reputation, supplies the pumps and other equipment that will handle the specified solvents and conditions, provides suitable monitoring instrumentation and expertise, and has the proper personnel protective equipment (PPE).
- Monitor and document contractor performance for compliance with the cleaning specification.
- If extensive tube replacement is being performed before the cleaning, consider an initial alkaline detergent cleaning step prior to the planned chemical cleaning. Some hydrostatic test pumps reportedly may be a source of oil contamination.
- Find and fix all leaky valves that are needed for system isolation before the cleaning.

The 2003 EPRI guidelines provide additional information on planning for chemical cleaning of HRSGs. $^{\scriptscriptstyle(2)}$

4.5 Chemical Cleaning Solvents and Procedures

As indicated in the preceding section, solvent selection options may be constrained and in some instances dictated by the hydraulic evaluation and cleaning system design options. When failing to make the hydraulic assessment the potential impacts are unknown and may lead to ineffective removal of deposits. The impact of possible hydraulic constraints should not be neglected when considering factors such as deposit composition and loading, cleaning schedule and time requirements, waste disposal options, and overall project costs.

The cleaning case studies also provided a number of additional suggestions which may aid in optimizing the performance of chemical cleaning procedures. Available operational cleaning experience clearly shows that approaches used for preoperational cleaning are unlikely to be suitable for removal of potentially heavy operational deposits. Operational chemical cleaning procedures can be improved in several ways; these include the following.

- Increased minimum contact times for iron oxide removal with the various iron oxide removal solvents can compensate for other factors (temperature and pH) which may be less than optimal.
- The temperatures for operational cleanings of HRSG units, generally, need to be higher than those used for preoperational cleanings.
- For diammonium EDTA cleanings, have formic acid on site to maintain solvent pH values in the desired pH range (5.0-5.5) so as to maintain rapid iron oxide dissolution.

- Track total calculated solvent concentrations (e.g., sum of free EDTA and estimated spent EDTA from iron dissolved) to determine when a solvent is uniformly distributed and the cleaning is complete.
- Following iron oxide removal with ammoniated citric acid, wait at least one hour following ammonia addition before applying the oxidant for passivation. Check the pH in all possible vents, drains, and deadlegs in the system before the initiation of oxidant addition. Continue to monitor solution pH during the passivation stage.
- Particularly if hoses are used in the cleaning system, be careful to add liquid to packed systems or nitrogen to the vapor space in the drum in nonpacked systems during periods of cooling to avoid the formation of a vacuum and the collapse of hoses.

4.6 Chemical Cleaning Deferment

Several measures have been used to defer the performance of chemical cleanings of some HRSGs. These include cessation of the use of duct burners and changes in cycle chemistry. Also, as presented in Section 3, mechanical deposit removal by hydrojetting has been used to avoid performance of chemical cleaning. The effective use of commercially available hydrojetting services has been limited mainly to units with tubes rolled directly into accessible upper and lower drums and which facilitate this type of operation. However, one facility with a HRSG of modern evaporator design with conventional harp assemblies elected to cut into the welded tube headers for videoscopic inspection and removal of localized deposits by hydrojetting rather than chemically cleaning the entire evaporator.

With each of these deferment options it is likely to be necessary to replace some HRSG tubes. (In one extreme instance (Case Study 13), the owner elected to retube the entire HRSG due to the extent of deposition and damage that had occurred.) If considering these deferment options it is very important to consider their applicability to and suitability for the HRSG design. Above all, these approaches should generally be regarded as deferment actions. For instance, cessation of use of duct burners may slow deposition and corrosion but such action places constraints on unit operation. Chemistry improvements without chemical cleaning can reduce feedwater corrosion transport and flow accelerated corrosion but will not totally arrest underdeposit corrosion at locations with heavy deposits where such mechanisms were active prior to the improvements. Mechanical removal of deposits by hydrojetting is not possible in HRSGs with complex circuitry unless steps are taken to provide access as was done in one case study when other work provided a means of access.

4.7 Conclusion and Future Needs

The data base assembled by the project team is not extensive and does not provide a sufficient level of information on operational cleaning experience to serve as a basis by which comprehensive revision of the 2003 chemical cleaning guides is justified. Compilation of the database of chemical cleaning case studies has shown a number of areas where deficiencies in the approach followed in many of the case studies assessed have resulted in less than optimal

cleaning experience; these findings have been presented as lessons learned. These lessons and any others learned from subsequent operational chemical cleanings must all be considered as input to future guidelines revision work.

The limited attention given to internal inspection of tube sampling of HRSGs for the case study population is generally consistent with practices of most organizations operating HRSGs in combined cycle and industrial cogeneration facilities. It is also understandable given the fact that methods developed and used in conventional boilers are not as compatible with HRSG designs. In recognition, EPRI has begun investigations of more suitable techniques for nondestructive examination of HRSGs. Work is also ongoing to develop repair techniques that better meet the requirements of HRSGs. As part of these activities it is intended to seek and develop new methods of assessing internal tube surface conditions that are either completely nondestructive or minimally destructive in nature that are better suited for HRSGs.

Of the case study facilities at which tube samples were collected, all reported evaporator tube deposit loadings values were significant and this impacted the chemical cleaning approach selected and implemented as well as the effectiveness of the cleaning in many instances. Available information for these case studies has indicated a number a factors which contributed to HRSG deposition and corrosion. These factors are not applicable to all HRSG installations. One important similarity is the widespread absence of data on internal surface conditions in tubing of evaporators and other HRSG circuits due largely to the challenges and costs associated with collection of tube samples. This lack of information is regarded as a source of some concern that, in the absence of cleanliness information the risk and incidents of corrosion damage and failures by mechanisms requiring internal deposits will grow over time. Also, the case study experiences clearly show that heavy deposits do not always lead to rapid corrosion damage due to the low temperatures and heat fluxes normally present in HRSGs. Overheating damage is not expected though possible when duct burners are included in the design.

Thus the need for revised and improved operational cleaning guidelines will become increasingly important. In most situations, approaches that were used to remove iron during preoperational cleaning are not likely to be effective if applied to heavy operational deposits. Further, the relative importance of factors influencing the need to clean, approach, cleaning time and costs for HRSGs will likely prove to be different than for conventional fossil boilers.

HRSG designs, as noted at several points in the various case study presentations, often place constraints on effective chemical cleaning. Known experiences with mechanical deposit removal by hydrojetting described in case studies in Section 3 are interesting. Further investigation of the possible use of cleaning by hydrojetting and possibly other nonchemical methods is needed to help define the applicability of such techniques as an adjunct to chemical cleaning or to defer performance of chemical cleaning.

4.8 References

- 1. Cycle Chemistry Guidelines for Combined Cycle Heat Recovery Steam Generators (HRSGs), EPRI, Palo Alto, CA: 2006. 1010438.
- 2. *Heat Recovery Steam Generator (HRSG) Chemical Cleaning Guidelines*, EPRI, Palo Alto, CA: 2003. 1004499.

Export Control Restrictions

Access to and use of EPRI Intellectual Property is granted with the specific understanding and requirement that responsibility for ensuring full compliance with all applicable U.S. and foreign export laws and regulations is being undertaken by you and your company. This includes an obligation to ensure that any individual receiving access hereunder who is not a U.S. citizen or permanent U.S. resident is permitted access under applicable U.S. and foreign export laws and regulations. In the event you are uncertain whether you or your company may lawfully obtain access to this EPRI Intellectual Property, you acknowledge that it is your obligation to consult with your company's legal counsel to determine whether this access is lawful. Although EPRI may make available on a case-by-case basis an informal assessment of the applicable U.S. export classification for specific EPRI Intellectual Property, you and your company acknowledge that this assessment is solely for informational purposes and not for reliance purposes. You and your company acknowledge that it is still the obligation of you and your company to make your own assessment of the applicable U.S. export classification and ensure compliance accordingly. You and your company understand and acknowledge your obligations to make a prompt report to EPRI and the appropriate authorities regarding any access to or use of EPRI Intellectual Property hereunder that may be in violation of applicable U.S. or foreign export laws or regulations.

The Electric Power Research Institute (EPRI)

The Electric Power Research Institute (EPRI), with major locations in Palo Alto, California, and Charlotte, North Carolina, was established in 1973 as an independent, nonprofit center for public interest energy and environmental research. EPRI brings together members, participants, the Institute's scientists and engineers, and other leading experts to work collaboratively on solutions to the challenges of electric power. These solutions span nearly every area of electricity generation, delivery, and use, including health, safety, and environment. EPRI's members represent over 90% of the electricity generated in the United States. International participation represents nearly 15% of EPRI's total research, development, and demonstration program.

Together...Shaping the Future of Electricity

Program:

Heat Recovery Steam Generator (HRSG) Dependability

© 2006 Electric Power Research Institute (EPRI), Inc. All rights reserved. Electric Power Research Institute and EPRI are registered service marks of the Electric Power Research Institute, Inc.

Printed on recycled paper in the United States of America

1012756

ELECTRIC POWER RESEARCH INSTITUTE