

Chemical Cleaning of Fossil Power Station Steam Generators; Past, Present and Future

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Technology for chemical cleaning of steam generators at fossil stations was developed during the latter half of the 20th century. Cleaning solvents and processes were developed for application to conventional boilers. The new fleet of combined cycle generating units with heat recovery steam generators (HRSGs) has raised questions concerning the applicability of technology developed for use in conventional boilers. Chemical cleaning technology is often regarded as mature; there is limited emphasis on research and development. However, there are challenges related to environmental, health and safety concerns, as opposed to technical efficacy. Meeting these challenges will require that new cleaning techniques be technically acceptable and cost effective.

1. Introduction

EPRI published a manual on chemical cleaning in 1984 [1] and has had cleaning guidelines for conventional boilers and other fossil plant components in place since 1993 [2]; a revision of the cleaning guidelines was published in 2001 [3].

Development activity and subsequent field application around the world led to some philosophical differences on how chemical cleaning of fossil plant steam generators should be approached. As the power production industry undergoes globalization, the need to understand differences in how chemical cleanings are approached has become more acute.

The applicability of cleaning technology developed for use in boilers of conventional fossil units to combined cycle generating units with heat recovery steam generators (HRSGs) has been a subject of debate.

Economic and environmental considerations have led some to question the necessity of preoperational cleaning of HRSGs. Limited experience and regulatory uncertainties make it unclear as what the future will hold with respect to operational cleaning. In 2003, EPRI published the first comprehensive guideline in the world for chemical cleaning of HRSGs and other components of combined cycle units [4].

2. Cleaning Solvents and Processes

Removal of iron oxides from fossil plant steam generators is typically accomplished with one of the following solvents, all of which have been used with success in conventional boilers:

- Hydrochloric Acid (HCl)
- Hydrofluoric Acid (HF)
- Hydroxyacetic-formic Acid (HAF)
- Ethylenediaminetetraacetic Acid (EDTA)
- Citric Acid (CA) Compounds

HCl has been widely used in preoperational and operational cleanings of conventional boilers. It has not been used extensively for preoperational cleaning of HRSGs, though it may be considered where needed for future operational cleanings. Although widely used for preoperational and operational cleanings in other countries, use of HF is generally avoided in North America. In North America, ammonium bifluoride (ABF) is frequently added to HCl solvent solutions; reaction of ABF and HCl produce some HF which enhances iron removal and allows solubilization of silicates in the deposit material. HAF is an effective iron removal solvent that exhibits low affinity for other deposit constituents. Historically, its use has been restricted to preoperational cleaning of conventional boilers and operational

cleaning of conventional once-through boilers; there are no known examples of its use in HRSGs. EDTA and CA formulations have been used for preoperational and operational cleaning of conventional boilers and are also suitable for application to HRSGs.

These solvents should be properly inhibited and may require inclusion of other chemicals—either to adjust the pH to that required by the process or to enhance removal of specific deposit constituents. For example, pH control of EDTA and CA is commonly accomplished by addition of ammonia to the solvent or, less frequently with CA, with sodium compounds. Also, a copper complexor such as thiourea may be added to HCl to enhance removal of copper and copper oxides. Table 1 summarizes the more commonly used solvents and application conditions [3,4].

Table 2 characterizes the affinity of these solvents for various waterside deposit constituents that may be present [3,4]. By inspection of the entries to Table 2, it should become clear that a deposit analysis is an integral part in planning operational cleanings of fossil steam generators. An iron concentration of 2.0% is generally regarded as the maximum safe level to avoid corrosion of the base metal in the steam generator. Multiple stage cleanings are typically needed in such cases. When heavy operational deposits are present, it is especially important to collect representative tube samples, perform a deposit analysis and perform trial cleanings in the laboratory to identify solvent characteristics and process conditions required for a safe and effective cleaning in the field.

Multistage cleaning may also be needed when the deposit contains appreciable amounts of copper and copper oxides, since the iron removal solvents all have, at best, only limited affinity for copper. Typically, ammoniated solutions with an oxidizing agent are used when a separate copper removal stages are required. Sodium bromate is a commonly used and effective oxidizer for this service. Gaseous oxygen is also effective in removal of copper at the deposit/solvent interface.

Sodium persulfate has also been applied as an oxidant for removal of copper from fossil plant steam generators.

The contact period for HF is generally very short when the steam generator deposits consist principally of iron oxides, whether in preoperational or operational cleanings. For operational cleanings of deposits with non-ferrous constituents, contact periods will also be brief, providing suitable solvent characteristics and process conditions can be established. This should, however be verified through laboratory evaluation.

Another important advantage of HF cleanings is the relative simplicity of waste treatment [5]. Typically, treatment of HF wastes is accomplished as follows. Lime is applied to adjust the pH to 6.5-9.0. (Neutralization results in conversion of the acid to calcium fluoride.) Powdered activated carbon is added to bind the inhibitor and any other organics, such as wetting agents that may be present. Following pH adjustment and oxidation, iron oxides and most of the calcium fluoride will settle out. The bulk of the liquid is removed by decanting while the remaining wet sludge is typically processed in a filter press or similar device. The liquid phase, after testing to verify compliance with local standards is generally suitable for direct discharge from the plant site. The sludge cake must be disposed of. In Europe, this is typically accomplished by either landfilling or incineration, depending on local regulations.

3. Chemical Cleaning Process Operations

Chemical cleaning procedures consist of a series of process operations, including the following [3,4] :

- Isolation of system to be cleaned
- Debris removal
- Hydrostatic testing and preliminary leak detection
- Superheater and economizer flushing
- Preheating and temperature control
- Solvent injection

Table 1. Summary of Typical Iron Oxide Removal Solvents

Solvents and Conditions of Use	HCl	HF	HAF	Ammoniated EDTA	CA (Citrates)	
					Ammonium	Sodium
Typical Use Concentration, %	5-6	1-2	3-6	4-6	2-6	2-6
Typical Use Temperature, °F (°C)	150-160 (66-71)	150 (66)	200 (93)	Iron: 180-200 (82-93) or 265-300 (129-149) Copper: <150 (66)	Iron: 180-200 (82-93) or 240-275 (116-135) Copper: <150 (66)	Iron: 180-200 (82-93) Copper: <150 (66)
Contact Time, Hours – Poor Circulation	4-6	Minimal	12-24	12-48	12-48	12-48
-Good Circulation	N.R.	Minimal	6-12	6-24	6-24	6-24

- Leak detection and response
- Solvent movement
- Monitoring of cleaning process
- Completion of cleaning
- Removing solvent
- Removing solvent
- Rinsing and flushing
- Neutralization
- Passivation
- Inspection of cleaned system
- Layup

Each operation must include adequate provisions for safety of personnel. More than one of the preceding operations may be accomplished in one step. For example, preoperational degreasing, millscale removal, neutralization, and passivation of HRSGs are all accomplished concurrently in ammoniated EDTA and citric acid cleanings. Every cleaning should be considered unique, and the series of operations which comprise the procedure should be modified as

necessary to suit the particular solvent used and prevailing conditions at the job site.

Requirements for solvent movement are diverse and vary with the particular solvent(s) selected for use in the cleaning. In the cases of EDTA, CA, and HAF, circulation of the solvent with pumps is the most common practice. Pumps are sometimes used with the copper removal solvents; movement may be obtained depending on the piping arrangements by either circulation of the solvent or partial draining of the solvent from the steam generator and subsequent reinjection.

Only limited solvent movement is needed with HCl; circulation must be limited because it increases the corrosivity of this solvent. In the case of steam generators with internal circulation pumps, periodic operation (generally no more than five minutes per hour) of one pump is typically practiced. In the case of steam generators without circulation pumps, the standard approach to solvent movement when using HCl is to practice periodic partial drainbacks of the solvent, followed

Table 2. Deposit Removal Characteristics of Typical Iron Oxide Removal Solvents

Constituents in Deposit: Capacity for Constituents in Question						
Solvents and Deposit Constituents	HCl	HF	HAF	Ammoniated EDTA	CA (Citricates)	
					Ammonium	Sodium
Iron Oxides	High	High	High	High	High	High
Copper, Metallic	Low ^a	Trace ^b	Trace ^b	Medium	Medium	Trace ^b
Copper, Oxide	Medium ^a	Trace ^b	Trace ^b	Medium	Medium	Trace ^b
Nickel Oxide	High	--	--	High	High	High
Zinc Oxide	High	--	--	High	High	High
Aluminum Oxide	Low	High	--	Trace	--	--
Chromium Oxide	--	--	--	--	--	--
Calcium Salts	High ^c	Medium ^c	Low ^c	Medium ^{c,d}	--	--
Magnesium Salts	High	--	Low	Medium	--	--
Silica	Low ^e	High	Low ^e	--	Low ^e	--
Carbonates	High	--	--	High	--	--
Phosphates	High	--	--	Medium ^d	--	--
Calcium Sulfate	Low	--	--	Trace	--	--
Organics	Trace ^f	--	--	--	--	--

^aWith sufficient copper complexor present – such as thiourea.

^bDissolved copper will redeposit as metallic copper on bare steel surfaces.

^cExcept for calcium sulfate, which is difficult to dissolve.

^dRemoval may require long contact time.

^eProvided ammonium bifluoride is added.

^fTrace materials may slough off during cleaning. Organic matter, when present, often carbonizes next to the metal surface and requires removal with an alkaline permanganate solution. Massive, short-term oil intrusion into the feedwater can result in oily deposits covering a mixture of carbonized oil and existing metal oxide deposits. Use of a strong alkaline detergent for removal of noncarbonized oil and prolonged exposure to strong alkaline permanganate solutions for removal of carbonized oil deposits may be necessary.

by immediate reinjection to minimize temperature losses. A less frequently followed approach is to periodically blow nitrogen into the lower headers of the steam generator. The effectiveness of this latter practice is often questionable since there is generally no provision made to control distribution of the gas within the steam generator.

When HF is used, solvent movement is the key to the ability to obtain rapid removal of deposit materials with this solvent. The approach taken to solvent movement when using HF is generally dependent on the design of the steam generator to be cleaned [6]. For once-through steam generators, pumps are used and a flow path is established that allows continuous injection of HF solvent and movement of the solvent through the steam generator. Injection of the solvent continues until chemistry readings indicate that cleaning is complete. Upon determination that cleaning is complete, HF feed is terminated and the system is flushed with water, after which ammonia and hydrogen peroxide are injected to passivate the metal surfaces. This approach to solvent movement is known as the open circuit (OC) technique. Figure 1 depicts a typical arrangement for preoperational cleaning of a once-through steam generator [6].

For the preoperational and operational chemical cleaning of plant equipment in Europe, feedwater pumps or boiler circulation pumps are not normally used because of possible warranty problems. For drum-type recirculating steam generators, an autocirculation (AC) technique employing injection of nitrogen is used to produce circulation in the evaporator and waterwalls. The density of the fluid is decreased by the injection of a proper gas-nitrogen or clean air (may be used during flushes and when degreasing but not with HF) to the suitable locations in the evaporator.

Independent of the type of construction, the gas is injected either to the downcomers or to the lower headers by the means of nozzles or special distribution systems. As the connecting point for the injection system in the headers, the inspection ports are used. For the injection into the downcomers, the existing drains or temporary connections are used. The other possibility for the gas injection is to establish temporary connections

to the drum, either through a temporary manhole cover or by dismantling of a valve on top of the drum.

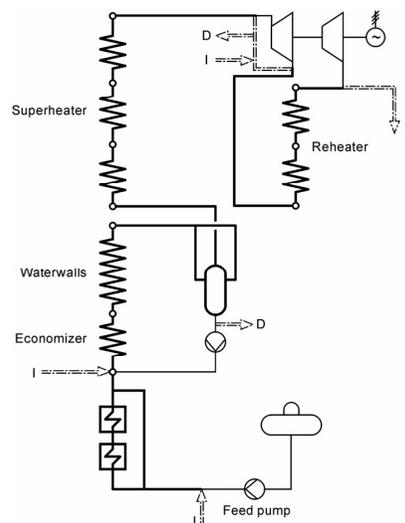


Fig. 1. Open Circuit (OC) Technique used with HF in Once-through Steam Generators

Circulation may be established in either the “operational” (natural circulation) direction or in the opposite direction. The injected gas is released via the drum vents. Figure 2 shows the AC technique with gas and solvent flow in the direction opposite to the operational circulation [4,6]. The quantity of injected gas is checked by flow meters.

Movement of solutions in ensuing discussions assumes application of the AC technique, as has been applied to HRSG systems with drum-type evaporator circuits. However, for conventional fossil units with once through boilers, it is customary to inject solvent with pumps, make a single pass through the boiler, and collect the solvent as waste material using the open circuit (OC) technique [4,6].

4. Assessment of Cleaning Requirements

Prospective chemical cleaning projects are evaluated with respect to two primary criteria: technical efficacy and cost. Technical efficacy

must consider compatibility of the solvents under consideration with the cycle materials they will come in contact with during cleaning and the effectiveness of the solvents on the specific deposit constituents of interest (see Table 2). For operational cleaning, it is generally advisable to assess technical efficacy in the laboratory by performance of simulated cleanings [1-4]. This requires collection of a tube sample and is typically accomplished by means of either immersion testing (Fig. 3) or use of a dynamic test loop (Fig. 4).

This is especially important in cases where there is little or no operational cleaning experience for the steam generator in question, the deposit composition is unusual, or deposit accumulations are considered to be heavy. Such testing activities allow the anticipated solvent composition and process conditions to be applied to a sample of the tubing that will be cleaned in the field. It also is useful in appraising situations (such as heavy deposits and/or high levels of copper in deposits) that multiple cleaning stages may be required.

Assessment of the cost of cleaning must examine three factors. The first is the cost of materials, equipment and labor required to perform cleaning. The second is the cost of steam generator downtime.

The third factor influencing the cost of chemical cleaning is the cost associated with management of wastes produced during the cleaning. Depending on circumstances, cost may be incurred for waste storage, transportation, treatment and disposal. Options for waste management are variable and dependent on the solvents and other chemicals to be used, national, regional and local regulations applicable to the plant site and plant design (which may or may not allow on-site treatment of wastes).

At sites that are not capable of directly handling the waste with on-site facilities, some provision for temporary storage is normally required [4]. As local regulations are always site-specific, it is always best to consult with local regulatory agency representatives regarding permissible designs or on site storage of

hazardous and non-hazardous wastes and associated containment requirements.

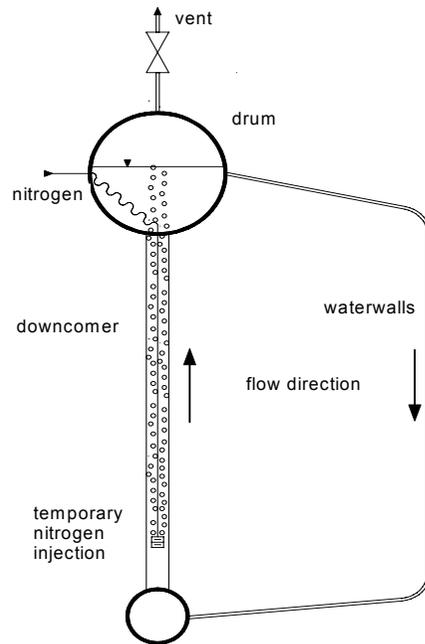


Fig. 2. Autocirculation (AC) Technique used with HF in Drum-type steam generators
Autocirculation (AC) Technique: Solvent Movement is Opposite Direction to Natural Circulation

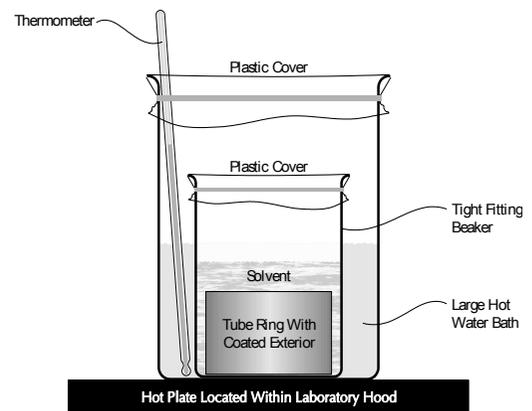


Fig. 3. Typical Laboratory Setup for Immersion Testing [4]

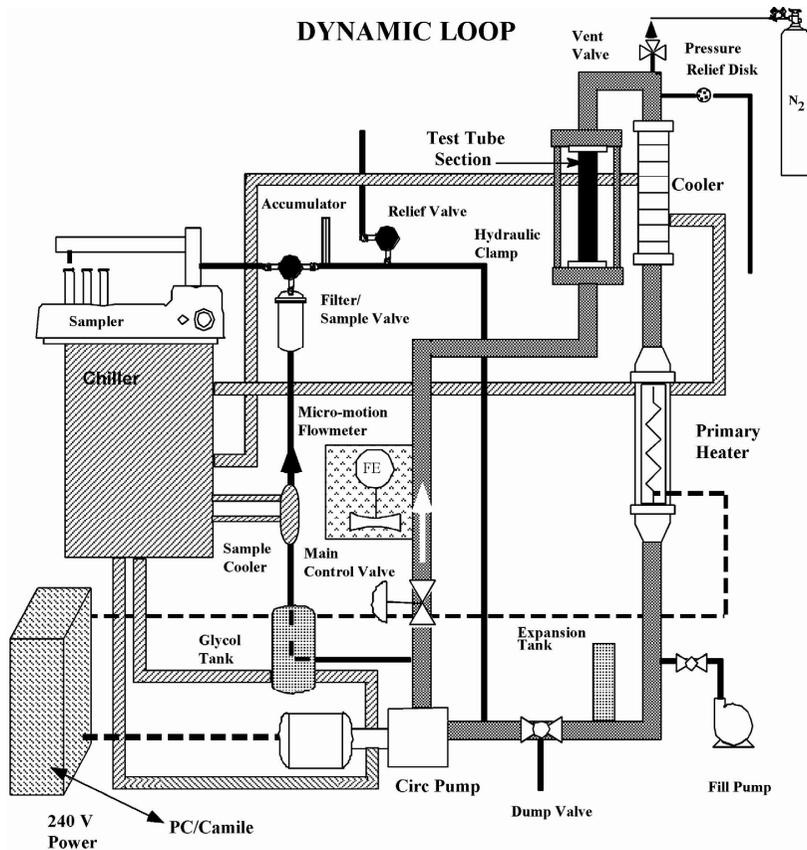


Fig. 4. Schematic of Dynamic Testing Loop [3, 4] Source: HydroChem Industrial Services

In North America, and possibly at other locations with oilfield operations in reasonably close proximity, it is most common to use portable tanks to accept and store the cleaning wastes. Mobile storage tanks with capacities of up to approximately 75,700 to 94,600 liters can be leased from cleaning contractors and other companies. A number of these tanks (commonly referred to as frac tanks) can be used to accommodate the first solvent drain since they can accept high flow rates and elevated temperature solutions which some collapsible tanks cannot. If the tanks are composed of lined steel, cooling of hot solvent may be needed to protect the lining.

If portable tanks are considered for use, it is necessary to determine by inspection that the empty tanks delivered to the job site are thoroughly clean. On a number of occasions,

chemical waste treatment operations have been seriously complicated due to the presence of other concentrated waste residues within the tanks when they were delivered to the generating station. Transfer of spent solvent solutions to such tanks can resolubilize residues and create problems during subsequent treatment or disposal operations. With this option, suitable steps must be taken to ensure containment, thus protecting the local environment from leaks and spills.

In locations where frac tanks or other portable storage devices are not readily available, other approaches to waste storage must be considered. The common practice of European chemical cleaning companies and also of the European steam generator suppliers for handling the waste from the preoperational and operational cleanings is to look for an easy, economical solution using

safe and suitable locations on site. One possibility is the use of existing equipment: pits, storage tanks, cooling tower basins. Materials must be checked for compatibility with the chemical(s) and temperatures used during the cleaning steps. If necessary, proper linings can be used to protect the surfaces of the equipment and also to make the cleaning of the equipment (after the waste treatment is finished) easier. Also, it must be verified that use of the existing equipment for temporary waste storage can be done safely and will not lead to violation of any regulations.

The other possibility is to prepare temporary pit(s) with sufficient volume to hold the complete chemical cleaning solution(s). Generally, a pit is excavated or an earth barrier is prepared, the ground is smoothed and consolidated with textile fleece as supporting layer. The plastic foil courses are shifted in such a way that they overlap and are joined with double hot-air welding seams, and tested with compressed air for tightness. A concrete plate in the basin serves as resting mounting plate for the discharge line and as impact plate for the waste solutions. For mixing of the wastes, an air distribution system is installed on the bottom of the pit.

The number of pits depends on the local environmental regulations on the discharged treated waste water; providing separate pits for different cleaning steps make it possible to treat the waste according to applicable regulations.

5. Research and Development Needs

The technology used for chemical cleaning has been under development for several decades. However, the future is likely to create incentives for improvements in this area. Continually tightening environmental regulations are expected to be a major factor requiring reassessment of old technology, resulting in either new cleaning methods or, at the very least, refinement of the process controls used with existing solvents. The desire to minimize operating costs is also expected to lead to future research and development activity in the area of chemical cleaning. This may be accomplished improved understanding of the relationship between

waterside deposits and steam generator thermal efficiency and tube corrosion, ultimately improving the understanding of how to optimize the interval between operational cleanings.

With regard to management of cleaning wastes, member organizations of EPRI have identified several areas of concern. These include:

- Release of solvent vapors, primarily of ammonia to the plant atmosphere; this issue could perhaps be addressed by improved vapor management strategies but ultimately could lead to evaluation of alternatives to ammonia based solvents.
- Improved and cost effective technology for on-site treatment of cleaning wastes; reducing copper concentrations in the liquid waste to levels at which discharge is allowable is typically a problem with on-site treatment.
- Varying regulatory policy with respect to disposal of certain cleaning wastes (mainly EDTA and CA) by injection into the furnace of the steam generator; a better understanding of the effect of such practice on heavy metals in the waste (particularly chromium) is needed.
- The method of injecting certain cleaning wastes into the furnace of conventional boilers is well understood and can be accomplished without causing damage to the boiler fireside; applying this method in HRSGs is unproven but could be useful to some organizations if it can be demonstrated to be effective and safe.

At one time, the chemical cleaning service companies had significant research capabilities and could have played an important role in addressing future challenges resulting from changes in environmental regulations. Today, however, these capabilities are, in general, substantially reduced. However, these organizations can still make a contribution in this area and will be integral to introduction and demonstration of new technologies.

The influence of steam generator waterside deposits on thermal efficiency is undeniable but has proven very difficult to quantify, at least in

conventional boilers, where performance is impacted by many factors. It has been suggested that it should be easier to correlate increases in HRSG evaporator deposits to efficiency decreases and performance losses. Ultimately, it may be possible to demonstrate this relationship and develop some criteria for operational cleaning that would cost effectively optimize combined cycle unit availability and performance. Improvements in this area will likely require the involvement of combined cycle plant operators and the HRSG manufacturers.

In conventional boilers, periodic operational cleaning is advised as needed to avoid conditions at which certain boiler tube damage mechanisms are known to become active and can thus lead to tube failures. These mechanisms all involve underdeposit corrosion activity and include hydrogen damage, acid phosphate corrosion, and caustic gouging. These mechanisms are also possible and have in fact been experienced in HRSGs despite the relatively low heat fluxes which typically exist in these units. While these mechanisms are very well understood, it is still not possible to quantify the deposit levels and boiler water chemistry conditions (particularly for hydrogen damage) at which underdeposit corrosion activity initiates. Ongoing research by EPRI is directed towards improving the understanding of these corrosion processes with the intention of establishing improved cycle chemistry control guidelines and chemical cleaning criteria.

6. Conclusion

The technology for chemical cleaning of fossil steam generators is well established and effective when selected and applied properly. While considered to be mature technology by many, it is quite likely to require changes in the future. Waste management concerns and desires to improve cycle performance and minimize fossil plant operating and maintenance costs are anticipated to provide incentive for future development.

Meeting the future challenges of chemical cleaning will require commitment on

various parties. Regulatory agencies must be part of the process so that future direction can be understood early and appropriate response strategies defined and implemented. Further, it is essential that these agencies have some fundamental understanding of the need for chemical cleaning and its impact on industry. Research organizations such as EPRI must take responsibility to assure that the needed work is identified early and can be completed in time to meet the needs of end users. Chemical cleaning service companies, steam generator manufacturers and the owners and operators of fossil generating plants will all play vital roles in assuring that this seeming mature technology area evolves as needed to meet currently anticipated-as well as unanticipated challenges of the future.

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