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Layup for Cycling Units: Requirements, Issues, and Concerns – An EPRI White Paper

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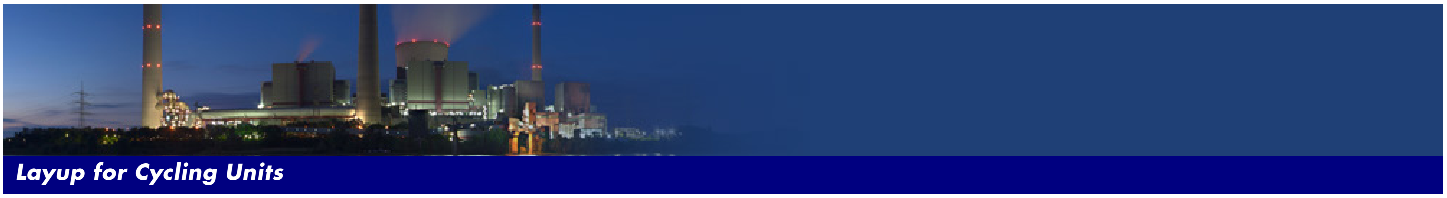

Abstract

The proper layup of the power generating water and steam cycles during periods of idle operation is a necessity—regardless of the duration of the shutdown or outage period. The duration of idle operation of these cycling units may range from a few hours to several days or more. Typically, these practices are not employed or are even ignored for units that are frequently dispatched to meet economic or seasonal load demands. This white paper describes the basic damage that results from poor protection during unit shutdown as well as practical techniques to address equipment protection. Frequent outages of short duration and the conditions prevalent on return to service during startup can seriously jeopardize the performance and availability of the unit. Prudent implementation of the practices described can greatly reduce the risk and improve the availability of the unit without jeopardizing the essential operating flexibility.

Keywords

Cycling
Equipment preservation
Flexible operation
Layup

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Foreword

Many of the failure mechanisms in boiler, superheater, and reheater tubes are initiated or exacerbated by poor layup practices. The effect of corrosion and deposition is well known and documented with regard to equipment reliability, availability, and equipment failures. Corrosion of idle components most often is a result of the corrosive environments provided by moist, aerated, stagnant conditions. Poor layup practices also contribute to inattention to the ingress of environmental contaminants and proper water / steam chemistry conditions.

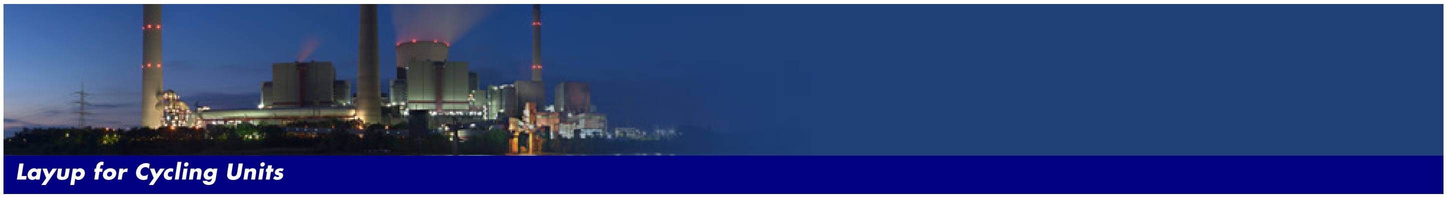
Placing units into hot or cold standby operational status for short periods of time when the generation is not needed is a common practice of economic dispatch for most utilities. This is typically a simple process which permits the equipment to be immediately available and placed into service in a matter of hours. Frequent short term shutdowns subject the metal components in the water /steam circuit to corrosive situations since the protection of the equipment rapidly deteriorates with loss of chemical control, ingress and exposure to atmospheric air, and condensation of moisture in normally dry regions. These events are frequently disregarded as insignificant or unworthy of remedial efforts due to the brevity of the situations and / or the need for rapid return to service. However such negligence is totally misguided as corrosive activity occurs most rapidly at the onset of exposure to the corrosive conditions and this action is usually compounded by the higher residual metal temperatures at local corrosion sites.

Methods and procedures to effect corrosion mitigation as a part of the shutdown and startup processes need not be cumbersome or capital intensive. In fact, some of the common sense methods outlined are less resource intensive than the "do-nothing" options and provide greater operating flexibility and more rapid response to generation demands. Effective shutdown and layup practices provide an excellent startup ability to rapidly achieve and maintain proper water chemistry conditions with minimum corrosion products.

Preservation methods must address the prevention and reduction of the deterioration of the major components using practical and efficient techniques requiring minimal equipment modifications and maintenance activities. Corrosion is the most serious form of deterioration.

The mitigation of corrosion in all parts of the water / steam circuit is achieved by applying one or more of the following actions to provide proper wet or dry conditions during standby operation:

- Elimination of moisture (water, humidity, and deliquescence of deposits/salts)



- Elimination of oxygen – minimize oxygen solubility or partial pressure; provide an inert (nitrogen) atmosphere
- Elimination of the simultaneous occurrence of moisture and oxygen
- Elimination of the concentration of electrolytes (ionic impurities) in aqueous or wetted conditions (i.e. high purity water).
- Providing proper corrosion inhibition (alkalinity and pH control) of aqueous solutions.
- Providing a physio-chemical barrier to prevent contract of moisture, air, or impurities with the metal or metal oxide surface.

The water and steam touched tubing of the boiler is not the only equipment affected by poor storage practices. The steam turbine left open to the atmosphere is often subjected to warm and humid conditions that promote pitting, particularly on the low-pressure turbine blade/disk surfaces), which are be precursors to stress corrosion cracking and corrosion fatigue. In cases where the turbine has been contaminated with corrosive deposits (e.g., following a condenser tube leak), corrosion can be rapid and severe. Likewise, feedwater heater corrosion of the steam side components generate massive amounts of corrosion products that are subsequently transported to the boiler or steam turbine creating thermodynamic inefficiencies and sites of future corrosion damage.

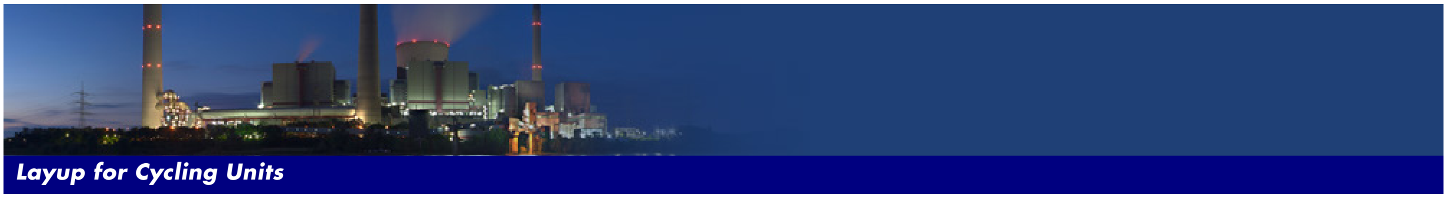
Use of drying methods, pH and water purity control, inert (nitrogen) atmosphere, and protective film inhibitors on metal surfaces can reduce or eliminate corrosion by controlling the amount of moisture available to support the chemical reactions of air (oxygen) and other corrodents, by eliminating oxygen and other corrodents, and/or by inhibiting the chemical reactions.

Introduction

For the purposes of this discussion, cycling units are those which frequently shutdown to zero power levels for short time intervals from as little as 8 hours or less up to 48 hours or more. Typically these units operate on a system load demand and/or economic dispatch which may be tied to conditions such as time of day, availability of renewal generation or alternate fuel / generation sources. Cycling units are most often required to be in a state of readiness for rapid return to service, i.e. fully available for dispatch with minimal notification. Accordingly, short term periods of 8-48 hours typically allow the unit to maintain sufficient heat to retain boiler pressure and turbine metal temperature and for the shorter periods even permitting extended condenser vacuum and cooling water circulation. These conditions all assist in the preservation techniques for the equipment. Certainly the layup and corrosion mitigation practices identified for cycling units are not limited to only those units of the foregoing description. Rather the layup practices and guidance are for those cycling units requiring the maximum flexibility for removal and return to service. It is recognized that there is no "one-size-fits-all" regarding the operating practices and procedures of units frequently cycled in and out of service or regarding the methods to be applied for optimum protection of all systems and components. Accordingly, the practices and recommendations for various unique operating/shutdown conditions are presented for the water/steam touched circuitry that will require some effort on the part of the plant operators to discern the most applicable practice or methodology for the various components and sub-systems of the individual situations. Depending on numerous factors these practices may not be the same from outage to outage but should always focus on the most practical and beneficial techniques to minimize equipment damage associated with out-of-service and standby operations. The preservation and corrosion protection during shutdown (i.e. layup) is only successful if the control measures implemented are effective and continuously and consistently applied. If several options are available certainly those providing the most practical and economic approach have advantages in situations of high frequency and often unplanned activity.

The purposes of layup practices are to mitigate corrosion damage of the cycle components and maintain the chemical integrity of the water/steam cycle during standby periods. Achievement of proper layup of the equipment and systems requires implementation of procedural steps during the unit shutdown and removal from service to eliminate and prevent introduction of corrosive conditions or environments. Accordingly, shutdown (and the subsequent startup) of equipment should be accomplished in a manner that does not subject the systems or components to an increased risk of corrosion damage; this would include such practices which induce increased localized stresses or increased concentration of contaminants or damage to the protective oxide which result in increased corrosion damage. Some of these unique events will be categorized.

The goal of a lay-up program is the same as the chemical conditioning program during unit operation: to prevent and / or control and reduce corrosion and the accumulation of deposits in the water/steam circuit of power plants. Optimization is most readily achieved when all conditions are at a steady state and equilibrium conditions can be established which are most favorable to corrosion and deposit prevention. Unit shutdown and startup by the very nature of these operations continually disrupt the established chemical equilibrium conditions within each circuit and between systems as a result of



changes in the thermodynamic conditions of temperature, pressure, and flow, as well as numerous physiochemical properties.

Water and steam circuit corrosion during shutdown is defined by the simultaneous presence of water and oxygen. If one or both of these can be effectively excluded, corrosion during layup is not reasonably expected. The methods of dry preservation (excluding water) and / or wet preservation (excluding oxygen) are based on these conditions. If these conditions cannot be fully avoided, methods of active or passive inhibition are required. Principally, inhibition is enhanced by the application of alkalizing chemicals to elevate the pH and provide the competing presence of hydroxide $[OH_-]$ to minimum concentrations to inhibit anodic corrosion – such as acid chloride conditions.

The selection of the layup and preservation methods depends on the circuitry and local conditions of the power plant systems and the duration and frequency of the shutdown. Although technically inappropriate, practical economic factors of assumed risk and asset value may dictate the choices and practices employed for layup during shutdown. The economic viability of such choices should be prudently evaluated; units of low capacity factors or limited service life may initially appear to be non-economically viable for minimum measures of equipment protection, however if this means units are unreliable or unavailable for service when needed this could alter the assessment.

As outlined, many of the practices for providing layup protection incur minimal costs; for example units with only seasonal demand stored following dry conditioning using methods of residual heat drying can require only procedural steps to preserve the greatest percentage of the water and steam circuits.

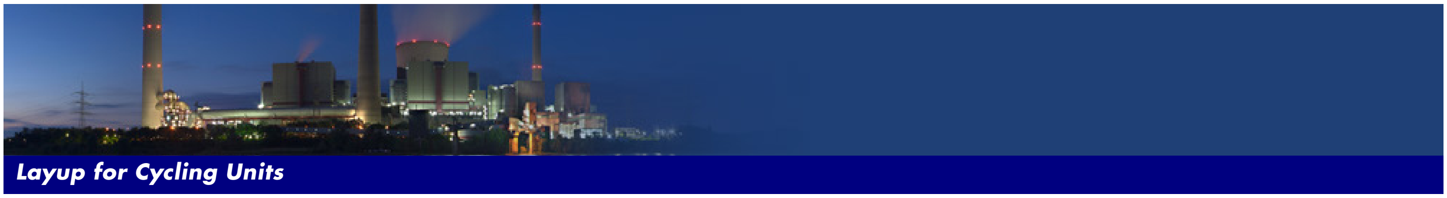
Corrosion Prevention and Mitigation

Corrosion is defined as the gradual destruction of materials, (usually metals), by chemical reaction with its environment. While this is frequently thought or assumed to be an oxidation of metals, in power plant water/steam systems corrosion is most frequently the result of the loss or destruction of the protective oxide on the metal surface which is a barrier to further oxidation and limits chemical attack. Passivation is an ultrathin layer of spontaneously formed oxide (magnetite, Fe_3O_4 on steel surface); the formation and stability of the passive oxide is a function of numerous environmental conditions.

In a dynamic/flowing aqueous system the most influential factors of iron oxide stability are the solution pH and oxidizing electrochemical potential (referred to as redox potential), temperature, the electrolytic strength of (electrical resistance or conductance), and the concentration of acidic or corrosive chemicals (e.g. chlorides, sulfates, etc. referred to as anions). With the optimum combination of these factors, passive oxide formation is enhanced and stabilized, whereas when these conditions are not maintained or other conditions exist the passive oxide can be destroyed and prevented from forming. One of the more familiar corrosion mechanisms illustrating destruction of the passive oxide and prevention of formation is flow accelerated corrosion in which insufficient pH and oxidizing power to maintain the stability of the passive film allows the dissolution of the oxide at a rate exceeding its stable formation and subsequent wastage of the metal. Note the corrosive attack of flow accelerated corrosion is not directly on the metal but on the stability and solubility of the oxide allowing it to be rapidly removed.

This basic understanding of the initiation of the corrosion process or the inhibition thereof is fundamental to the provision of layup protection of all the metal components in the water/steam cycle. Passive oxide and passivation is not just a boiler tubing phenomena, all metal (iron, copper, aluminum) surfaces possess protective oxides. This includes condenser and feedwater heater tubes, valves, pumps and piping, boiler metal and turbine blades. When the passive oxide is maintained corrosion and chemically induced damage mechanisms including pitting, corrosion fatigue and stress corrosion cracking, as well as general metal wastage are thwarted.

The corrosion of metal typically follows an electrochemical process in which electron transfer and mobilization of metallic ions (electrically charged molecules / atoms of soluble metal or metal oxides) occur in an aqueous medium (electrolyte). The electrolyte content of aqueous medium (water solution) consist of all the dissolved chemicals (salts) which exhibit an electrical charge (ions) and include alkalization agents and acids as well as neutral pH compounds such as sodium chloride (NaCl), metallic ions, and some dissolved gases (CO_2) The electrolyte content is important to the corrosion process and is determined roughly by the electrical conductivity of the water (µS/cm). The presence of the ions, their type and concentration not only elevate the conductance of the electrolyte which significantly increases the rate of ion transfer and corrosion, but also may directly participate in the electro-chemical corrosion process. Even in the presence of proper alkalizing (pH) inhibition the increased concentration of impurities and chemical contamination accelerates the corrosion process. Corrosion prevention in aqueous environment requires minimizing the electrolytic content (i.e. high purity water) and establishing conditions which are favorable to the maintenance of a stable metal oxide passivation.



Highly concentrated electrolytic solutions also develop in areas of "dry" deposits. Chemical deposits in the "dry" regions of superheaters, reheaters, and steam turbines may consist of various chemical "salts" (e.g. sodium phosphate, sodium chloride, ferric sulfate, etc). At operating temperatures these compounds are dry and do not form electrically charged ions that promote electrochemical corrosion. However, these compounds have the ability to absorb atmospheric moisture (deliquescence) at ambient temperatures (below the boiling point or "dew" point of the substance) and form high concentrated local solutions. Formation of hygroscopic deposits during operation is problematic during unit shutdown unless these areas can be maintained dry or exposed to very low humidity.

It is not only the changing solution chemistry that presents a threat to the integrity of the passivity of the metal surfaces, although solution chemistry is a major concern. Physical stresses brought about by temperature and pressure changes produce localized defects in the uniformity of the passive oxide structure. Coefficients of thermal expansion of the protective oxides and the underlying base metal differ and lead to fissures in the physically weaker structure. The temperature where the greatest dissimilarity of the expansion or contraction between the metal and the oxide can often be problematic especially if the rate of transition through the temperature range is too rapid to permit acclimation to the altered conditions. A common analogy is the rapid heating and cooling of glass, the greater the distortion of the temperature the greater the likelihood of cracking.

The significance of the defect in the passive oxide is that the metal surface at the defect location is exposed to the environment. While the environmental conditions may not be overly aggressive, all of the corrosion potential is focused on the minute local site at the point of the defect in the passive layer. Corrosion at these isolated areas is greatly amplified as access to the solution environment is restricted and the concentration gradient between the defect area and the oxide surface become greatly exaggerated and an electrochemical cell is established where the metal is rapidly corroded. A common example is oxygen pitting in which the isolated cell at the location of the oxide defect is deplete of oxygen but the surface is strongly passivated by the presences of high oxygen concentration. The defect area is highly anodic and corrodes (relatively) vigorously with the development of a pit.

Pitting

Pitting is localized part- or through-wall dissolution of tube metal. It is an insidious form of damage because a relatively small amount of metal loss can lead to through-wall failure with catastrophic results. Pitting can occur throughout the boiler or heat recovery steam generator (HRSG). Pitting can occur as a result of poor shutdown practices with low pH, oxygen-saturated, stagnant water and/or as a result of carryover of Na_2SO_4 into reheaters, which combines with moisture from condensation to form an aggressive chemical agent.

Pitting occurs during unprotected shutdown periods, not when the unit is operating. During shutdown, fluids left remaining are often stagnant and open to the atmosphere; under these conditions, they become saturated with oxygen. The fact that the fluid is static allows the initiation of pitting to occur unimpeded, and the stagnant conditions allow for the concentrations needed to accelerate the attack. Pitting and other localized corrosion processes such as crevice corrosion involve selective breakdown of the normally passive film on the metal surface. Chloride ions as well as low pH conditions chemically induce breakdown of the passive layer, which results in pitting corrosion; other anions (negatively charged ions) also contribute to low pH conditions capable of attacking the passive film. Chloride [Cl^-] ions are more mobile than competing hydroxide [OH^-] ions and readily penetrate the imperfections in the protective oxide, pit, or crevice leading to aggressive acidic conditions in these isolated regions and progression of corrosion and pitting damage. Accordingly elimination of oxygen and elevation of pH also require minimum chloride concentrations to fully diminish pitting activity. Conversely the simultaneous existence of these conditions promotes rapid pitting corrosion.

Prevention of pitting damage requires the use of appropriate shutdown and layup procedures and practices that prevent oxygenating the shutdown fluid and prevent aggressive chemistry and low pH conditions. Alternatively the metal surfaces must be kept dry and clean. Dry metal surfaces and environments of less than 40% relative humidity eliminate corrosion; the corrosion process involves the exchange of "soluble" ions to and through an aqueous environment. Without the aqueous media, these ions have no mobility to transport to and from the corrosion site and the corrosion process ceases. However "dry" residual deposits on the surface of the metal may create sites of local corrosion damage by directly absorbing moisture from the air (hygroscopic properties) to form extremely concentrated and corrosive droplets. In similar fashion the process of drying equipment will evaporate the water chemical solutions to create very concentrated and corrosive salt solutions with sufficiently high boiling points that the solution does not go to total dryness. Both conditions can promote localized corrosion.

For short-term layups, keeping high quality water with the same potential as during operation and without oxygen along with pro-

tective blanketing with nitrogen are recognized practices of protection. High purity minimizes the risk of chlorides or other chemical agents acting to degrade the protective oxide or corrode the metal. Maintaining a constant electrochemical oxidation-reduction potential is necessary to avoid changing the oxidation state of the protective oxide; the process of changing the oxide state produces a meta-stable oxide which is non-protective and can promote surface attack. Elimination of oxygen and prevention of the introduction of oxygen minimizes the pitting potential, as well as other corrosion mechanisms in a stagnant environment.

Layup Practices

From the previous discussion it should be obvious that layup involves those practices which will contribute to the elimination of corrosion mechanisms prevalent during periods of unit shutdown. While the optimum conditioning for each component in the water/steam cycle is achievable using methods of nitrogen (or other inert gas) blanketing, pH adjustment, and/or humidity control (dehumidification) these techniques often require special steps and equipment isolation that preclude having optimum flexibility of unit operation. For cycling operation there are some critical conditions that should be considered to improve the layup practices and lower the risk of damage. Greater details for proper layup are given in EPRI reports 1015657 *Cycling, Startup, Shutdown, Fossil Plant Cycle Chemistry Guidelines for Operators and Chemist*, 2009; 1010437 *Cycle Chemistry Guidelines for Shutdown, Layup, and Startup of Combined Cycle Units with Heat Recovery Steam Generators*, 2006; and 1014195 *Shutdown Protection of Steam Turbines Using Dehumidified Air*, 2008.

Addressing the necessity to maintain optimum unit availability and responsiveness to generation dispatching requirements while optimizing operations to provide layup protection to cycling units requires some practical and innovative methods which differ from the "established" practices but focus on the same "end effect".

Preboiler Water Circuits

Wet layup of the pre-boiler circuit provides water chemistry conditions that are similar to the conditions during plant operation. Wet layup in the feedwater and condensate system equipment consists of filling the components and connecting piping with treated demineralized water with low dissolved oxygen (DO) (less than 10 ppb) that contains the proper chemicals for the metallurgy of the system (all-ferrous or mixed metal). The equipment is completely filled (water solid) with the treated water to avoid pockets of trapped air, and is not open to the atmosphere.

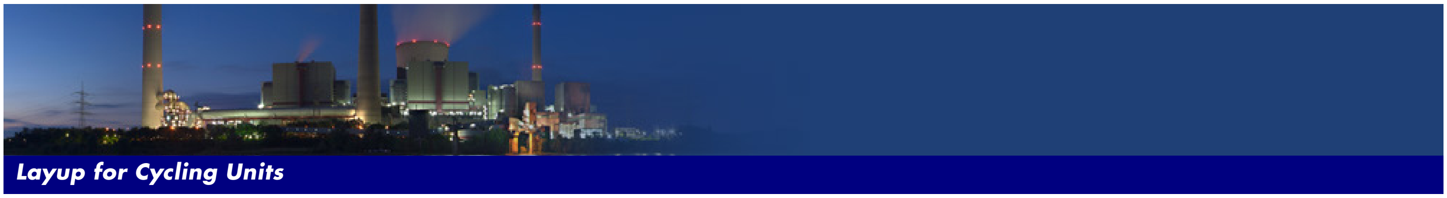
For cycling units layup of the preboiler circuit is straight forward. The pH of the water in the circuit is the same as during operation or slightly elevated using the same chemicals. The oxygen is reduced to levels of less than 10 ppb where achievable and for mixed metallurgy systems using a reducing agent the reducing agent residual is increased up to several hundred ppb. The system is kept water solid to preclude any introduction of air. None of the other methods of lay-up are practical or plausible for cycling units – nitrogen capping, or draining dry are not amenable to the circuit configuration.

The challenges faced by cycling units, as with all units, with this scenario is that as simple as it sounds, the achievement is quite complex. During the shutdown and coast down of the unit, the condenser performance for air removal and deaeration declines such that dissolved oxygen levels in the condensate escalate. Once steam flow to the condenser is discontinued the vacuum conditions and air removal is virtually loss and condensate is fully aerated. Similarly, following depressurization of the unit the deaerator in the circuit ceases to function and sometimes acts as a source of aeration. Flow through the circuit is still required to fill the boiler or maintain the liquid volume as a result of the contraction during shutdown and cool down of the components. The conditions lead to unacceptably high oxygen levels for shutdown and unit storage in the preboiler circuit (even units practicing oxygenated feedwater treatment require low oxygen for wet layup storage).

Chemically reducing oxygen with the addition of reducing agents (inappropriately referred to as oxygen scavengers) is ineffective and for all-ferrous circuits can be detrimental to the protective oxide. With mixed-metallurgy units the use of excess reducing agents promotes unacceptably high ammonia concentrations on the subsequent startup and dangerously high corrosion of steam side copper components.

pH control of the preboiler circuit is frequently lost during unit shutdown as a result of increased levels of carbon dioxide from air entrainment and increased make-up to the cycle with air saturated water. Make-up water is untreated (no pH adjustment) and aerated. The preboiler circuit serves as the conduit to transfer make-up water to the boiler or evaporator to supply the void created by the thermal contraction of the water.

Recognizing the importance of layup and stabilization of the iron oxides (corrosion products) in the preboiler circuit of cycling units takes into consideration that these units spend a disproportionate amount of time in shutdown and startup operations. Consequently the opportunity for excessive transport of corrosion products to the



steam generating equipment is greatly enhanced leading to excessive deposition and associated damage.

Approaches to layup and preservation of the pre-boiler circuit to address these challenges (and possibly those of the subsequent startup) include:

- Hotwell bubbler for oxygen removal incorporates a steam (possibly nitrogen) sparging/bubbling system near the hotwell outlet to strip non-condensable gases from the condensate. Steam sources during/after shutdown include LP heater extraction (prior to shutdown), steam drum as unit depressurizes, or steam header from adjacent unit or auxiliary system. Nitrogen can similarly be used but the consumption rate may be excessive.
- Steam or nitrogen sparger in the deaerator storage tank. This option offers great advantages on startup not only for deaeration but for pre-heating the boiler feedwater to minimize thermal differentials at the economizer inlet or boiler water downcomer.
- Minimum flow circuit from the economizer inlet or deaerator outlet to the condenser hotwell or condensate pump's suction. This permits hotter water to circulate through some deaeration devices as described or even to incorporate a side stream deaeration device, possibly as gas transfer membrane, to maintain low oxygen content. Periodic circulation (using condensate pumps or an external pump) eliminates areas of stagnation reducing pitting potential. The small loop provides a means of sampling for chemical analysis and for addition and mixing of treatment chemicals. Side-stream filtration/demineralization are facilitate with a low flow loop.
- Closing the deaerator vent prior to shutdown to prevent the introduction of air into the cascading water. Maintain steam pressure or nitrogen to maintain the vapor space if possible. Isolate the deaerator from the storage section and condensate as a means to prevent oxygen introduction to the preboiler circuit (typically not viable due to lack of automatic valves and valve sizes)

These approaches are not all encompassing but provide an indication of potential applications to enhance layup of the preboiler circuit and promote a more trouble free startup as well.

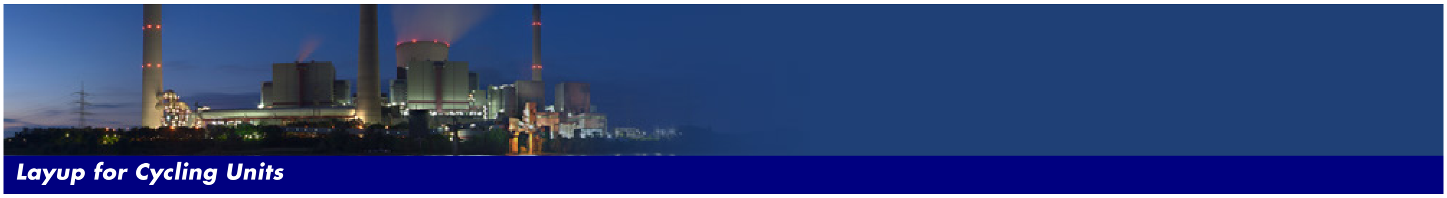
Boiler Circuit

The wet layup method with a steam or nitrogen gas blanket above the liquid level in the component or piping is highly applicable to the boiler circuit (similar to the deaerator discussion). This method is used for the duration of the outage for periods of several weeks where maintenance is not needed. Naturally, the first choice for a cycling unit not requiring boiler maintenance is to shutdown with an optimum chemistry condition by proper adjustment of the pH, and maintain steam/boiler pressure until the need for return to service. Following the eventual loss of steam pressure (unless supplied by an alternate source or unless re-firing of the unit) an inert gas (nitrogen) is supplied to collapse the residual steam at pressures around 25 psig and exclude the introduction of air during the cool down period and the collapse of the vapor. The main advantage of wet layup with a steam or nitrogen blanket is it eliminates the air / water interface eliminating localized pitting at the interface and the introduction of dissolved oxygen into the boiler water.

During the unit shutdown the blowdown of the boiler or evaporator is increased to lower the level of corrosive impurities in the boiler water. Reduction of impurities and in particular chloride, as previously noted, is critical to corrosion protection during stagnant periods. Research has clearly demonstrated that the corrosion and pitting potential are greatly reduced with higher purity water with lower concentration of aggressive chemical species. Similarly research has demonstrated that the concentration of aggressive chemical species in and beneath boiler deposits (and underdeposit corrosion) is reduced by purging of the boiler water (i.e. improving the purity of the boiler water on shutdown promotes "leaching" of contaminants from deposits and lowers the risk of underdeposit damage).

The makeup water to the boiler circuit(s) is high purity condensate/feedwater, properly deaerated (oxygen free) and of the proper pH. Make-up water is required to the boiler circuit until ambient temperature and pressure (except for steam or nitrogen blanketing) is reached. Additional makeup is continuously required if the boiler is purged or blown down during the shutdown period. Makeup can be suspended if the water level is not required to be maintained (provided air is still excluded by steam or nitrogen pressure).

The pH of the boiler circuit is maintained principally through the addition of a volatile alkalizing agent such as ammonia. This is because addition of tri-sodium phosphate at lower temperatures and pressures will not equate to the target pH at higher boiler pressures and an overfeed will result in phosphate hideout on the restart of the unit. Likewise there is a risk of overdosing sodium hydroxide. As the pressure of the circuit decays, a higher proportion of the volatile ammonia will distribute to the vapor phase and the boiler/evaporator water pH decreases. Sampling determines if additional chemical to maintain the pH is required. Units using phosphate treatment may experience a pH depression on unit shutdown due to possible phosphate hideout return. This condition requires elimination of the excess phosphate (blowdown or draining) and restoration of the pH with ammonia (or possibly low dosage of caustic). Maintaining



and/or elevating the pH of the boiler water is most critical during shutdown, layup and startup operations to mitigate corrosion fatigue in areas of thermally induced stresses.

Cycling units rarely afford the opportunity to completely drain and dry the unit, however draining with a nitrogen cap is a very satisfactory layup method provided the residual moisture (steam and water) have sufficient purity and pH to sustain corrosion inhibition. Similar to nitrogen blanketing, the boiler is drained while still having a steam pressure in excess of 25 psig and the nitrogen is applied to maintain the pressure throughout the drain and the subsequent cool down to ambient temperature. In locations where freeze protection is required this is perhaps the methodology of choice if supplemental heating is not supplied.

Nitrogen blanketing or purging requires temporary connection or properly engineered systems, as well as the additional nitrogen cost. The nitrogen, while typically injected in the vent connections can be introduced below water level even in downcomers, lower headers, or drain lines as long as there is an unrestricted flow into the vapor space. Nitrogen introduced in lower headers promotes mixing and deaeration in addition to the inerting atmosphere at the water vapor interface. The gas bubbles migrating through the boiler tubes or downcomers expand as they migrate to the surface promoting water movement similar to the thermal cycling of a natural circulation unit; the water weight in tubes with nitrogen is lower resulting in a natural circulation. The mixing also assists in providing representative samples of the water chemistry.

With the exception of the above criteria, preservation of the boiler circuit does not afford many other options. Making the unit water solid would include fully flooding the superheater, this is unattractive for cycling units which need a quick response. Likewise draining and drying the boiler (emphasis on drying) is time consuming and leaves the boiler space full of air which will inevitably mix with the water introduced to the boiler for startup. High oxygen in boiler water on startup is a leading contributor to corrosion fatigue damage. Where water is added to a drained boiler (not nitrogen blanketed) filling from the bottom of the boiler upward with deaerated (and pH adjusted) water drives the more aerated water ahead in the circuit such that the most highly aerated water is in the drum. Wasting some of the water through the drum blowdown can eliminate some of the most highly aerated water (however the vapor space is still full of oxygen). Heating the water to near saturation (212°F/100°C) for filling reduces the saturation of oxygen.

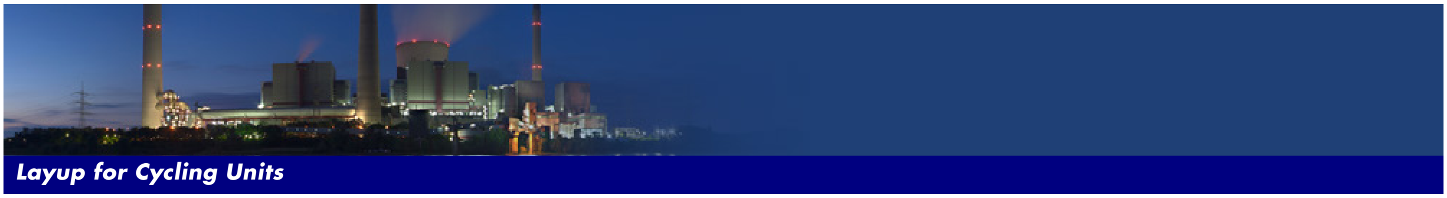
Reheater – Turbine Circuit

The practice for turbine layup is only dry storage. Similarly the reheater which receives only steam and is quickly evacuated on shutdown is most simply stored dry. As described previously, reheaters and turbines are subject to deposition of “dry” chemical compounds during normal operation which may be hygroscopic at ambient conditions and form aggressive chemical solutions on shutdown. These areas are naturally exposed to the steam vapor on shutdown unless specific actions are taken to eliminate the moisture fraction through purging and drying. Condensate formation in the reheater (similarly in the superheater) provides not only the mobilization of soluble chemical deposits, but allows the solubilization of oxygen when exposed to ambient air as the unit depressurizes. In the vertical tubes of the reheater (as well as the superheater) excessive condensation accumulates in the lower tube bends after collecting on the tube walls. The resultant solution accumulating in the tube bends contains remnants of the soluble deposits “rinsed” from the tubes. Subsequent dry out of pools in the tube bends concentrates the material and increases the likelihood of higher corrosive environments developing during succeeding layup periods.

There are techniques for nitrogen capping reheaters which incorporate applying nitrogen to a vent or drain while hot and isolated from the turbine/condenser and maintaining until the system is needed or until ambient conditions are reached.

Water soluble turbine deposits can be “washed” during unit shutdown using special operating techniques to lower the amount of superheat in the incoming steam to produce a “wetness” factor in excess of 3% throughout the turbine set. Nucleation of moisture droplets in the wet steam and the formation of liquid films on the metal surfaces will solubilize the “water soluble” deposits to form weakly concentrated solutions that are harmlessly rinsed and carried away. These practices require careful monitoring to assure the moisture and liquid are effectively removed so as not to leave highly concentrated residual. Wet steam washing of HP turbines should consider use of cold reheat drains to prevent carryover of contaminant rich liquid to the reheater.

Dry storage typically would mean the application of dehumidified air to capture all the residual moisture. The dehumidified air is applied in a fashion to assure a pathway through the entire turbine flow path including, if practical, the reheater. The moisture laden air is purged from the cycle – typically at the condenser until the desired level of humidity (typically <35-40%) is reduced and then the cycle is closed to incorporate a continuous flow of air through



the circuit. From a practical standpoint the dehumidification system is not engaged to the circuitry until the unit has moderately cooled.

An alternative approach is to maintain the condenser vacuum (including the cooling water circulation) once the generator is disengaged and pull vacuum through the turbine set and the reheater. Cautiously clean dry air (ambient relative humidity <40% - use a desiccating gel if needed toward the end) is introduced through the cold reheat piping to purge the residual vapor and produce dry conditions. The volumetric conditions of the vapor in the reheater and turbine set at the elevated temperature present only a fraction of the air requirements needed at ambient conditions to purge the circuit. Once purged, only a sufficient flow to prevent moisture laden air in the condenser from entering the LP turbine is necessary. In addition the warm air from the reheater (specifically the outlet steam header) and IP turbine set assist in maintaining LP turbine temperatures near 150°F / 65°C for several days. Oxygen solubility decreases at higher temperature and the oxygen solubility is sufficiently low at temperature above 150°F / 65°C to limit pitting of turbine components.

To facilitate lower moisture introduction from the condenser, the cooling water is maintained to lower the vapor pressure in the condenser. Unfortunately this has the effect of increasing the oxygen solubility in the condensate in the hotwell. Accordingly a continuous flow of dry air through the LP turbine set is prudent unless efforts to drain and dry the condenser are used.

Condenser and Shell Side Feedwater Heaters

Layup protection of the steam extraction from the turbine to the condenser and feedwater heaters is problematic for units not planning extended layups. The problem is that these are areas where residual moisture is present even when/if drained and are not (normally) isolated from the turbine set. Nitrogen application to feedwater heaters necessitates closing of extraction valve prior to loss of vacuum. This is typically not a considered option – especially for units expecting to frequently cycle.

Dehumidified air can be used to promote drying of the drained components. This technique requires draining and circulation of dry air until all the residual moisture is removed. Where dehumidification (including the modified technique outlined for drying the turbine set) is applied through the turbine distribution of air through the extraction lines and feedwater heater and subsequent drain piping may be insufficient for drying. In addition even the high pressure heaters have little residual heat upon shutdown because of the “cold” condensate and feedwater temperatures. Even with condenser vacuum the movement of dry air through the heaters is questionable.

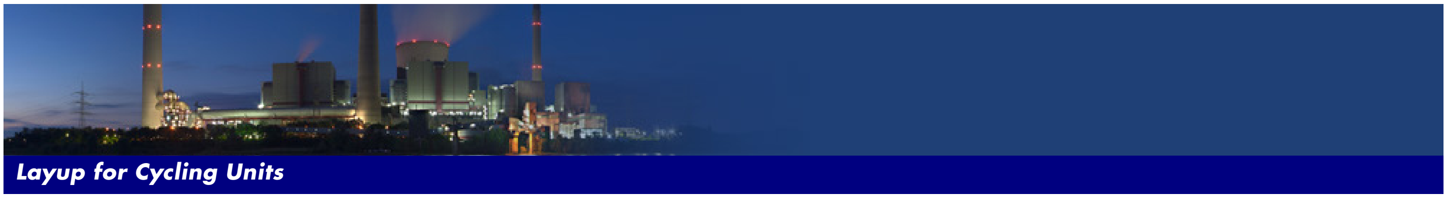
For cycling units layup of these components are extremely troublesome – not only are the techniques and method to accomplish preservation untenable but these components represent some of the largest surface areas of low alloy carbon steel and/or copper alloy material. Stainless steel components are subject to similar pitting as turbine blade materials. High corrosion product transport (iron and copper) in the feedwater on startup have been traced directly to condensers and shell side feedwater heaters. The corrosion rate of materials (specifically copper and copper nickel alloys and carbon steel) in the shell (steam) side of feedwater heaters is significantly accelerated during cycling service as a combination of poor lay-up practices and thermal cycling of the material.

Feedwater heater tube corrosion and failures associated with unit cycling and improper layup not only are major sources of corrosion product transport and deposition in boilers and turbines; major tube failures can lead to water induction to the operating turbine with devastating and catastrophic results.

Copper nickel alloys (70-30, 80-20 Cu:Ni) used for feedwater heater tubes exhibit extreme exfoliation on the external surfaces of the tubes associated with cycling and improper layup. Exfoliation, a type of intergranular corrosion at the grain boundaries resulting in a de-lamination of copper and nickel oxides, has been found to occur only in the presence of oxygen which is the critical component of the exfoliation-corrosion mechanism. Other copper alloys exhibit similar exfoliation behavior including alloys of >20% zinc and some aluminum brasses (but usually at higher temperature). Introduction of oxygen (air) into the heated wet environment of feedwater heaters on shutdown promotes rapid oxidation of the susceptible copper and nickel components.

Experience has shown that the exfoliation in cycling units is effectively resisted if heaters are blanketed with nitrogen to exclude oxygen when the unit is out of service. Although manufacturer O&M manuals provide instructions on shellside blanketing, nitrogen will flow to the turbine and condenser unless extraction valves are closed. To assure effective blanketing, nitrogen must be applied before discontinuing condenser vacuum. Once the vacuum or steam pressure conditions are lost, atmospheric air will be drawn into the feedwater heater vapor space.

Techniques of wet storage of the shell side of feedwater heaters has been suggested, however such practices require extreme caution



to prevent thermal transients from cooler water quenching steam extraction lines and water entering the turbine. As with nitrogen blanketing, wet storage of the shellside of heaters would be applied prior to discontinuing condenser vacuum by filling through the heater drains with chemically treated and deaerated feedwater or condensate similar to the wet storage of the condensate/feedwater circuit. During unit startup, the water is drained to the condenser or even to waste.

Protective Barrier Films

The most effective approach to equipment protection normally is to provide dry conditions. There are treatments that provide equipment protection by establishment of a barrier between the oxide surface and any water or moisture that may be present. Among these barrier treatments are vapor phase corrosion inhibitors, known also as vapor phase inhibitors (VPI), and filming amines, also referred to as film forming amines or polyamines. The method of protection of both of these barrier forming treatments is quite similar. The products have a chemical structure which contains both hydrophilic and hydrophobic sites. These features of the molecule provide an attachment or adsorption of the hydrophilic site to the surface of the metal (or metal oxide) in a monomolecular layer. The non-attached hydrophobic portion of the molecule repels the moisture (water molecule) and as the molecules accumulate the surface becomes non-wettable effectively providing a protective barrier to contaminants such as oxygen, water, and corrosive vapors. Since the molecules tend to repel each other, there is not a tendency for the accumulation of multiple-molecular layers or thick films.

The application methodology is quite different for VPI and filming amines. Since VPI compounds must be added after the equipment in removed from service and cooled, this technique is not viable for units of cycling service and short term outage.

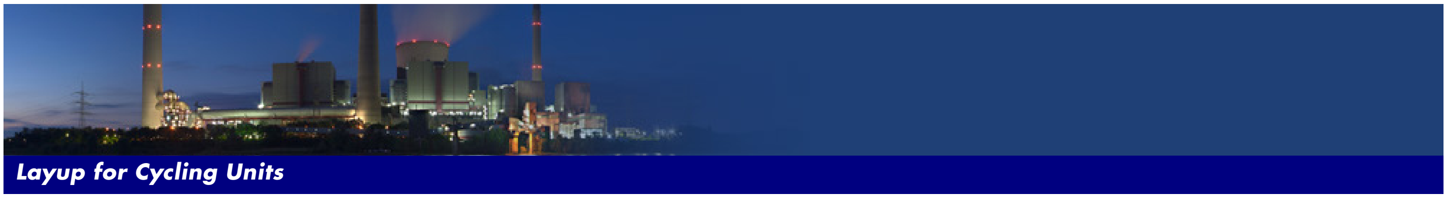
Filming (or film-forming) amines are typically used to counter the effects of oxygen corrosion and have been used as a means of equipment protection during both operational and idle conditions. Filming amines are long chain hydrocarbons that have one hydrophobic end and one hydrophilic end that form a monomolecular "film" on metal surfaces. The resulting film, similar to an oil or wax film, creates a physical barrier that prevents the water, oxygen or other corrosive agents from reaching the steel surface which aids in the protection of condensate/feedwater piping and steam generating equipment. The hydrophobic alkyl group of the amine makes the metal surface unwettable and once formed a protective film remains intact even after the dosage has stopped.

EPRI is working to develop a filming inhibitor method which has found favorable application in other power generating circuits – namely in China, but also in Russia. The filming inhibitor forms a bond with iron (Fe) atoms on the metal surface. The hydrophobic film has a physical shielding effect from the corrosion medium, and inhibits the corrosion on the surface of the metal. EPRI research has demonstrated the effectiveness of the application of filming amines for the inhibition of pitting and crevice corrosion of turbine steels and the marked reduction of material wastage by single phase FAC.

The filming inhibitor is added into the water/steam through a chemical addition system prior to the unit shutdown. The amine travels through the entire water/steam cycle and gradually forms the protective film on all the metal components in the cycle. The film is stabilized and maintained by establishing a residual concentration in water and steam in combination with other water treatment chemicals. Due to steam volatility of filming amines, film formation also occurs on metal surfaces of the steam and condensing systems including the turbine, superheater and reheater, feedwater heaters and condenser. The protection is present in both the wet and dry conditions including those exposed to humid aerated environments.

The use of filming amines needs to be judicious. Insufficient application can result in increased localized corrosion in areas of inadequate inhibition. Excessive dosing may have some unwanted effects and possible sloughage of iron deposits or sludge formation. Some impacts on analytical measures have been noted with excessive use of filming amines. Condensate polisher resin fouling does occur with the use of filming amines; condensate polishers should be bypassed and removed from service during dosing of filming amines for layup.

For a sufficient application, enough filming amine must be applied to provide uniform coverage of all the water and steam touched surfaces. Coverage requirements are expected to range from 10 to 50 milligrams per square meter of surface area (10–50 mg/m^2). This can be a significant quantity of product since the surface area of a typical coal fired unit can range 50,000 to 100,000 m^2 (500,000-1,000,000 ft^2) depending on the unit generating output, volume, and design. In addition a minimum residual of 0.25 to 1 ppm (part per million or mg/liter) in water or steam is required to maintain the surface coverage. The initial dosing concentration must be greater than 1 to 5 ppm or more in order to provide the necessary concentration gradient for rapid development of the protective film. These dosages and concentrations refer to the filming amine molecules (i.e. 100% filming amine). The actual dosage and coverage requirement will vary depending on the actual filming amine compound and/or formulation. The filming amine products as supplied by the manufactures are typically very dilute and



knowledge of the supplied concentrations will be required in order to calculate the proper dosages.

Conclusion

Wet layup of the preboiler and frequently the boiler is the most practical approach for cycling units. pH adjustment and elimination of oxygen are the prime requisites for wet layup application. This means complete deaeration of the condensate and feedwater and prevention or air entering the boiler and superheater. Nitrogen blanketing and / or maintaining boiler pressure is required to prevent introduction of air. pH adjustments need to assure all the liquid (including condensed steam in the superheater) is equal to or in excess of normal pH conditions.

Use of filming amines as a corrosion inhibitor has been shown to enhance the wet layup practices in all parts of the water / steam cycle. Filming amine dosing of the entire circuit in advance of shutdown acts to supplement wet layup methods and provides corrosion inhibition in addition to reducing the corrosion reactions.

Dry storage is the best (and proven) option for the reheater and steam turbine. Residual heat of the turbine is generally sufficient for maintaining a “dry” conditions for periods of 24-36 hours, but condensation and oxygen will initiate corrosion once a relative humidity greater than 40% or the “dew point” temperatures are reached. Reheaters that are force cooled require immediate purging of steam vapor since exclusion of oxygen laden air in difficult to achieve. Dry reheaters, like the turbine, are subject to condensation and aeration on cooling.

Condensers and shell (steam) side feedwater heaters are very difficult to provide corrosion protection. These components frequently are the major areas of corrosion during unit shutdown and the source of deposit forming corrosion products during startup. The options for proper storage of this equipment is more limited.

Filming amines may provide an alternative for the dry regions of the reheater and turbine and for the moist and wetted regions of the condenser and feedwater heater. Applied during operation in advance of shutdown film coverage of the wetted and dry components make the surface unwettable and resist corrosion. This methodology represents a significant advancement to layup for cycling plants. Layup with filming amines presents no disruption (except as noted) to the operation of the unit and in fact enhances both the equipment protection and the rapid return to service.

Using practical methods as outlined to address corrosion concerns procedural practices can be effectively put in place that will provide optimum corrosion control of cycling unit without jeopardizing flexible or increasing operating costs.

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