How Repeat Situations Lead to Chemistry-Related Damage in Conventional Fossil and Combined Cycle Plants

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ABSTRACT

The scientific understanding of most forms of chemistry-related damage in conventional fossil steam-water cycles and combined cycles with heat recovery steam generators (HRSGs) is very advanced and has been so for many forms of damage for more than 30 years. In spite of this, chemistry-related damage and the cost of availability losses related to deficient chemistry practices are often enormous. Damage and component failure incidents persist, in both fossil units and combined cycle units. Further, much of the damage is reported to be caused by damage modes that are well known and documented. It is thus very clear that the approaches taken by organizations operating fossil units to prevent such damage are frequently unsuccessful. Similarly, fossil industry usage of the response methodology by which chemistry-related damage events are reacted to (identification of the mechanism, assessment of the root cause, and implementation of actions to stop the mechanism) is often ineffective. Recent analysis of past cycle chemistry assessments and damage/failure proactively. This involves identifying repeat cycle chemistry situations which are allowed to continue by the chemistry staff or are imposed on the plant/organization as a consequence of inadequate management support for cycle chemistry.

INTRODUCTION

Across the worldwide fossil fleet, damage and failures involving the cycle chemistry continue to dominate the scene within many organizations despite a concerted effort to improve the scientific understanding of such damage through targeted research and dissemination of this information to end user organizations. In existing conventional units, the approach has been to respond reactively to damage/failure events so as to understand them and stop their occurrence whereas in the relatively new combined cycle fleet, application of "lessons learned" was considered an appropriate means of eliminating many chemistry-related problems during unit design.

The reality of the situation becomes readily apparent when past and present fossil industry performance is considered. Cycle chemistry accounts for about 50 % of all forced outages of fossil units and their major components. In the combined cycle fleet, it appears this figure is closer to 70 %.

Boiler tube failures (BTFs) and heat recovery steam generator (HRSG) tube failures (HTFs) serve well to illustrate the point as they represent, overall, the most prevalent cause of forced outages across the industry. However, some units experience very few chemistry-related tube failures while in others they happen frequently and are often the leading type of damage. A 2007 survey [1] confirmed that chemistry-related BTF (<u>Table 1</u>) and HTF (<u>Table 2</u>) mechanisms are still commonly experienced by many end users. It is important to note that the chemistry-related failure mechanisms indicated in these tables have been well understood and thus controllable for many years. Conversely, many of the same chemistry-related mechanisms have been commonly observed as long as statistics on cycle chemistry in fossil units have been collected.

Similarly, the majority of failures of steam turbines can be related to the cycle chemistry (<u>Table 3</u>). Single-phase flow-accelerated corrosion (FAC) damage activity is dependent on the feedwater chemistry [2].

Continuation of these trends is reinforced because cycle chemistry problems are usually of a longterm nature whereas financial performance typically has a short term (commonly a fiscal year) focus. The critical influence of the chemistry is often not recognized when assessing unit and equipment availability and efficiency and when evaluating forced outage rates. Only a small minority of utility organizations around the world are known to properly assess the influence of chemistry on the overall cost of unit operation. Thus many proposed chemistry improvements are rejected on economic grounds due to short term costs-to-benefit analysis whereas the longterm value of the unit as a generating asset is reduced.

Mechanism	Chemistry-influenced?
Fly ash erosion	No
Corrosion fatigue in sub-critical waterwall tubes	Yes
Sootblower erosion	No
Longterm overheating (high temperature creep) in SH/RH tubes	No
Underdeposit corrosion mechanisms	Yes
Hydrogen damage	
Acid phosphate corrosion	
Caustic gouging	
Pitting in RH tubes	Yes

Table 1:

Leading boiler tube failure mechanisms.

SH superheater; RH reheater

Mechanism	Chemistry-influenced?
Flow-accelerated corrosion in low pressure evaporators (single and two-phase damage)	Yes
Thermal fatigue (economizer/SH/RH) and creep fatigue (SH/RH)	No
Corrosion fatigue in low pressure (LP) evaporators and economizers	Yes
Underdeposit corrosion in HP evaporators	Yes
Hydrogen damage	
Acid phosphate corrosion	
Caustic gouging	Yes
Pitting	Yes

Table 2:

Leading HRSG tube failure mechanisms [1].

Mechanism	Chemistry-influenced?
Corrosion fatigue of blades and disks in phase transition zone (PTZ) of LP turbine	Yes
Stress corrosion cracking of discs in PTZ of LP turbine	Yes
Pitting	Yes
Copper deposition in HP turbine	Yes
Liquid droplet erosion	No
Flow-accelerated corrosion	Yes
Deposition of other impurities	Yes

Table 3:

Leading steam turbine damage mechanisms.

ALLOWING REPEAT CYCLE CHEMISTRY SITUATIONS TO CONTINUE WILL EVENTUALLY LEAD TO CYCLE CHEMISTRY-INFLUENCED DAMAGE AND FAILURE

The authors have just re-analyzed a large number of cycle chemistry assessments, boiler and HRSG tube failures, steam turbine blade and disc failures, numerous FAC incidents and benchmarking processes for cycle chemistry and boiler tube failures. These have been conducted in over 100 organizations around the world that utilize a variety of chemical treatments and control limits. There are two key results of this analysis which relate to why and how failure/damage occurs in fossil and combined cycle/HRSG plants. The first shows that any cycle chemistry-influenced failure involves the breakdown of the protective oxide which grows on all fluid-touched surfaces. This could involve cracking, fluxing, dissolving, and solubilizing of the oxide layers. This will be the topic of a parallel paper. The second clearly demonstrates that every cycle chemistry failure/damage can be related backwards in time to situations which were not recognized or properly addressed and allowed to repeat. In some cases the chemistry staff did not recognize the importance of the situation and allowed it to continue. In other cases the chemistry staff recognized the importance, but was not successful in convincing the management (either plant or executive) that action was required. In many cases the management has delayed action or has not provided the necessary funds to resolve the situation. There are also many cases where immediate action is not taken due to the commercial need to keep the unit running and, after a time, the repeat situation becomes accepted as normal, thus diminishing or negating the importance of the need for action. In doing this type of retroactive analysis it very quickly becomes obvious that plants/organizations can get away with having one or two repeat situations, but once this number increases then failure/damage is a certainty. Here actions that may be viewed as seemingly unrelated to chemistry should also be pointed out, such as a change in the furnace firing system design, which aggravated the distribution of boiler deposition (as summarized in Case Study 2 but an action common to numerous fossil boilers). This change rendered some tolerable but undesirable repeat situations associated with the chemistry program completely intolerable.

The authors' event analysis indicates that the following ten *Repeat Situations* exist and are very commonly associated with preventable cycle chemistry-related damage in fossil plants:

- High levels of corrosion products.
- High boiler/high pressure (HP) evaporator deposition.
- Non-optimum chemical cleaning.
- Contaminant ingress (with no reaction by the operators).
- Drum carryover.
- High level of air in-leakage.

- Lack of shutdown protection.
- Inadequate on-line alarmed instrumentation.
- Not challenging the status quo.
- No action plans for any of these repeat situations.

The authors feel it might be instrumental in helping organizations to avoid continuation of repeat cycle chemistry situations in the future if a few notes on each of the situations are provided here to ensure the nuances of each are understood. Examples of some of the typical repeat situations observed are given later in the paper by review of a few case studies to further illustrate this new concept.

High levels of corrosion products Almost all cycle chemistry guidelines (EPRI, VGB, JIS, Russian, Chinese, etc.) around the world include a suggested level of corrosion products for conventional and combined cycle plant feedwater and for evaporator circuits in HRSGs. These levels are attained by correct implementation of the feedwater treatment approach appropriate for the unit. (The preferred treatment approach is subject to change over the life of the unit though this is not always recognized or acted upon.) Not checking to determine if these levels are being met or allowing plant to operate with considerably higher levels is a classic repeat situation. The eventual result will be heat transfer surfaces having deposits which can be the centers for underdeposit corrosion, pitting and overheating. Each one of these damage mechanisms requires a second or third repeat situation to occur.

High boiler/HP evaporator deposition The corrosion products will eventually deposit on heat transfer surfaces and it is reasonably well understood that these can be harmful if contaminants or inadequate control chemistries are also allowed to exist (repeat situations as well). Most but not all conventional plants are cognizant that tube samples should be periodically removed and analyzed for deposit density. The same level of cognizance does not exist yet in the combined cycle/HRSG world. One repeat situation for either plant is not taking the samples frequently enough or from the correct area. Another is not using the information to determine when the deposits should be removed. Another involves the inadequate analysis of the samples removed. Probably the worst is when the management (plant or executive) decides that a chemical clean cannot be fitted into the outage schedule or that funds are not available to pay for it.

Non-optimum chemical cleaning Delaying of a boiler (or HRSG) chemical clean when a clear deposit density situation exists is a tremendous risk for the plant and has resulted in numerous subsequent failures and damage. Even when cleanings are performed as needed, deficient practices may exist in planning, performance, and post-cleaning inspection activities. The correct approach must be taken to assess the cleaning approach (solvent, inhib-

itor and additives, plus process conditions), plan the work, monitor the cleaning, and verify that the cleaning was successful, both in removing the waterside deposits and also in leaving the unit in a condition suitable for safe return to service. The approach followed must consider additional aspects including proper isolation of the system for cleaning and performance of flushing, rinsing, and draining. It should also allow for inspecting equipment to verify that all chemical and loose solids have been removed prior to returning the unit to service.

Contaminant ingress (with no reaction by the plant or operations) Contaminant ingress is unavoidable; given the right circumstances and time in space it will occur! In general, organizations are very aware of the potential harm that can be done by a large contamination incident. Conversely, many organizations are not aware that small contamination events, over time, can have detrimental impacts as well. A false sense of confidence often follows the minor contaminant ingress events early in the life of the unit that are not responded to quickly leading to an incorrect conclusion that they can be ignored when they occur again.

In many organizations recognition of when contamination occurs and provision of the required reaction is a paramount philosophy of the cycle chemistry program. However, there are too many examples of where the contamination incidents are so bad and frequent that they exceed the shutdown limit of a unit numerous times per year, and are ignored with no operator action taken. Another associated repeat situation within this category is the inadequate on-line instrumentation, or having the required instrumentation which isn't alarmed. Finally, the lack of action on the part of the operators or chemistry personnel can allow apparent ingress to persist, thus increasing the time during which damage occurs.

Drum carryover Very few organizations check drum carryover although it is a very simple and required process. Some of those that check carryover only do so at one of the multiple saturated steam off-takes. In older units, it is very common to observe that several of the off-takes have not been maintained and are no longer operable. Some don't realize the importance of carryover activity, which can change for various reasons until deposition is found on the steam turbine or maybe a phase transition zone blade fails. A case study example is included later.

High level of air in-leakage It is now well understood that for different reasons all combinations of plant materials (all-ferrous, mixed-metallurgy) and cycle chemistry treatments require the air in-leakage to be regularly measured and effectively controlled so that the oxygen at the condensate pump discharge is generally less than $10 \ \mu g \cdot kg^{-1}$. Each day this is not done represents a repeat situation that will have ramifications which depend on the plant materials and the treatments. In cycles with mixedmetallurgy feedwater systems increased air in-leakage in the presence of ammonia results in non-optimal protection of the copper materials and transport of copper to the boiler. At drum pressures above 16.5 MPa (2 400 psi) copper will carry over and deposit on the high pressure section of the steam turbine. Air in-leakage also contributes carbon dioxide, which will increase the measured cation conductivity, thereby making this key chemistry control parameter a less reliable indicator of cycle contamination by chloride and sulfate.

Lack of shutdown protection The interfacial science of failure/damage clearly indicates that most of the cycle chemistry-influenced failures including many of those noted in Tables 1–3 are associated with pits, which can only initiate and grow under the conditions of unprotected shutdown of pressure circuits. The most recent of these is the occurrence of stress corrosion cracking (SCC) and corrosion fatigue (CF) in the phase transition zone (PTZ) of the low pressure turbine, which is directly controlled by the lack of shutdown protection. So each time a unit shuts down without protection (nitrogen, dehumidified air, etc.) this is a repeat situation which furthers the unit along the path to failure/damage.

Inadequate on-line instrumentation So many of the incidents re-investigated involved a plant not having an adequate level of instrumentation such as the fundamental level of instrumentation in use by the authors. Many units continue to operate without any steam monitoring. It's amazing how often the inadequacy of this repeat situation occurs in parallel with one or more of the following repeat situations: no steam monitoring when drum carryover is high, no cation conductivity monitoring on the boiler water when small condenser leaks occur, or instruments on overhaul or "tagged out" when an acid excursion takes place. In other examples the operators decommission audible alarms because of unrealistic limits. It is no coincidence that a combination of these repeat situations and actions is associated with chemistry-related damage.

Not challenging the cycle chemistry treatment status quo This is probably one of the most frequent repeat situations. The authors visit too many plants where failure/damage has occurred simply because the chemist or management has not challenged the suitability of the operating chemistry since the unit was new. Changes in chemistry may be needed due either to improved understanding of chemistry treatments and their applicability to various types of plant, or to changes to the unit design or operation. Combined cycle/HRSG operators continue to get some confidence level out of operating with a reducing agent despite a clear relationship with the occurrence of FAC. Conventional plant chemists continue to operate with antique phosphate treatments when these have been shown to clearly lead to failure when other repeat situations are allowed to exist and continue. This includes making unsafe/unjustified changes in the chemistry (Case Study 1), using control limits that are not optimal (Case Study 2), and using treatments in units where they are not needed and can actually increase levels of corrosion products (Case Study 3). In other instances, the correct chemistry is selected but not fully optimized (Case Study 4).

No action plans for repeat situations Once the plant operators, chemistry personnel, and management recognize damaging repeat situations it is then necessary to initiate action to address them. This is often difficult for the chemist to accomplish on his own for two main reasons: a) his/her (low) position within the plant, and b) many of the repeat situations in this list are not under the chemist's control (e.g. air in-leakage and implementation of shutdown protection). Formalization of the strategy and resources required to correct the repeat situation in the form of an action plan is a proven means of chemistry improvement with support across the organization. The optimum process is to have these repeat situations, including development of action plans, incorporated into the combined corporate or plant directive for boiler or HRSG tube failure reduction (BTFR and HTFR) and cycle chemistry improvement (CCI). This is described later in the paper.

In the absence of a proactive policy on chemistry, as formalized through issuance of a corporate directive or similar document as discussed later, acceptance of detrimental repeat situations often becomes part of the culture of the organization. In part this is due to the myopic view of financial management and some chemistry staff. It is exacerbated by the tendency to perceive these situations as acceptable, since they typically individually do not have any short term consequences. Thus, the associated costs of avoiding these situations are often deemed unnecessary despite the negative value over the operating life of the asset. This factor continues as older units reaching the end of their originally intended operating life continue to be relied upon to meet system demands for power.

In many instances this perception has been transitioned from the older conventional units to combined cycles. Thus the opportunity to avoid many cycle chemistry problems has been lost in the name of minimizing the capital cost. During early operating life, the operating practices frequently follow those followed in the conventional cycles, which means that undesirable repeat situations are established from initial commercial service. Additionally, deficient chemistry practices required during unit commissioning are continued by the owner. These cost impacts are often overlooked as it is part of the unit operating and maintenance costs.

An important aspect of cycle chemistry repeat situations in fossil and combined cycle/HRSG plants is that they can continue to be recognized reactively when a cycle chemistry assessment is being made or failure/damage has occurred. In the authors' opinion there is no doubt that every cycle chemistry damage/failure event can be related back to repeat situations. However, it appears much more powerful for organizations to try to deal with these proactively. Case Study 3 which follows illustrates this aspect of repeat situations in a combined cycle plant. They can also be dealt with proactively in conventional fossil plants by incorporating them into the plant directive for BTFR and CCI, and including them in the goals of the plant management.

CASE STUDIES OF DAMAGE INVOLVING REPEAT SITUATIONS

To illustrate the powerfulness of identification of repeat situations as a proactive assessment tool to avoid damage, some representative case studies from over a hundred cases the authors have been involved in over the last ten years are outlined here. In each case it will be seen that several repeat situations have been allowed to continue.

Case Study 1: Steam Contamination

Protection of steam turbines from chemistry-related damage has long been recognized as an integral aspect of effective cycle chemistry programs. Equipment manufacturers and research organizations have performed extensive investigations of damage mechanisms and determined that most are related to the chemistry, both during operation and when the unit is out of service.

Experience has shown that many organizations continue to experience contamination of the steam, leading to various consequences. In some instances, a developing problem is identified during service, but in many cases, the existence of steam purity issues only becomes apparent during an inspection conducted as a scheduled maintenance activity or as a consequence of a failure incident. As a case in point, the following Case Study illustrates a pattern observed that in some respects is very similar to occurrences in other fossil plants around the world. It began with an outage inspection for a conventional fossil unit during which the steam drum interior did not exhibit the customary waterline. Further, white deposits were observed, in this particular instance in a boiler operating on caustic treatment (CT). Subsequent inspection of the low pressure turbine determined that no stress corrosion cracking damage (SCC) was present. However, pitting of surfaces in the PTZ was observed; pitting is known to be a precursor to possible future damage by either SCC or corrosion fatigue (CF). The condition of the blade attachment areas remains in question.

Further review and discussion uncovered additional information relevant to this specific case. The boiler operating pressure at the drum was well in excess of 17.2 MPa (2 500 psi), which is generally accepted as the maximum safe pressure at which to employ CT. The normal rate of caustic feed to the boiler was increased for some time (months) prior to the outage; it was thought that this increased demand for chemical was due to the development of a small boiler tube leak. This assumption was accepted within the plant and other possible causes of chemical loss from the boiler were not considered.

Drum carryover testing was not performed prior to or after introduction of CT nor at any other time since commissioning of the unit. The provided steam samples had not been available for some time prior to the outage, thus there was no direct indication of the steam purity. However, the condensate sodium analyzer indicated readings higher than normally observed. Outage activities identified a problem with the steam drum level measurement equipment. Actual drum levels were determined to be somewhat higher than indicated to plant operators. When considered collectively, it becomes very easy in retrospect to see why a situation of boiler carryover and steam path contamination developed.

For most species in the boiler water, mechanical carryover is the predominant means of transport to steam. The primary exceptions are copper compounds and silica, which exhibit significant volatility, even at low pressure. Sodium hydroxide exhibits nearly no volatilization tendency, meaning that vaporous carryover is insignificant and thereby placing importance on the ability to know the boiler mechanical carryover for individual steam generating circuits. This relationship is well understood. For example, the International Association for the Properties of Water and Steam (IAPWS) has considered the issue of drum carryover and recently decided to provide the industry with support in the form of an IAPWS Guidance document [3].

In this particular instance, four repeat situations were present and allowed to continue. The first situation involved continuing to operate without any steam purity information owing to all of the steam samples being out of service. The second situation was the failure to challenge the status quo specifically by not assessing boiler carryover, which amounts to an acceptance that the original carryover test results were still valid many years later. Such assumptions are particularly cavalier when applying CT at largely untested and potentially unsafe drum pressure levels. The third repeat situation relates to the absence of adequate shutdown protection for the steam turbine. Pitting within the turbine arises during unprotected shutdowns and any contaminants (particularly chloride) in the steam which deposit within the PTZ exacerbate pitting. The fourth repeat situation resulted from acceptance of the incorrect assumption that a boiler tube leak accounted for loss of chemical from the boiler and, as a result of failure to consider other possibilities, an absence of any action until inspection findings revealed a different sort of problem in need of attention.

Units with significant drum carryover which are subject to acceptance of these repeat situations often suffer consequences in the form of turbine damage with either blade damage or damage to the blade attachments. Also, it should be understood that the repeat situations noted here are generally involved in the development of other chemistry-related steam path damage events including deposition in superheaters and reheaters, dissimilar metal weld damage, and high pressure turbine deposition.

Case Study 2: Underdeposit Corrosion Damage

Boiler waterwall tube underdeposit damage mechanisms include acid phosphate corrosion, which requires deficient phosphate treatment, caustic corrosion, which requires deficient control of the sodium hydroxide dosing, and hydrogen damage, where contaminant levels sufficient to corrode the protective oxide layer develop. High levels of waterside deposits are also required for these damage mechanisms to become active. Each of these mechanisms has also been observed in high pressure HRSG evaporator circuits.

Hydrogen damage remains a very prevalent damage mechanism even though it is fully understood and the conditions needed to cause it and ways to prevent it from recurring are well known. The mechanism habitually troubles a number of organizations, plants and specific units. In looking at a large number of hydrogen damage events over several years, the pattern that emerges becomes very clear and always includes a number of repeat situations, many of which are not properly addressed, thus keeping the door open to further damage events in the future.

A recent hydrogen damage failure event investigated by the authors serves as a good illustration of the trend that is very common across the fossil industry. Consideration of the root causes of damage determined that nine of the ten repeat situations existed to varying degrees:

- High levels of corrosion products: available results of analysis for iron and copper in the boiler feedwater during service confirmed that each was typically much greater than the achievable levels associated with optimized chemistry treatment programs.
- High boiler/HP evaporator deposition: the boiler in this unit accumulated waterside deposits rapidly, requiring frequent chemical cleans.
- Non-optimum chemical cleaning: periodic tube sampling to track deposit growth and plan for cleanings was not being practiced. Spool pieces were not used during cleaning and post cleaning tube samples were not collected.
- Contaminant ingress (with no reaction by the operators): condenser leaks had become accepted as part of normal operation, with chemical additions to the boiler increased to reduce pH depression. The operators had no further direction in response to contaminant ingress to the boiler.
- High level of air in-leakage: condensate dissolved oxygen levels in the unit were consistently in the range

30-80 μ g · kg⁻¹ and there was no active effort to find and resolve cycle air in-leakage.

- Lack of shutdown protection: no protection plans were in place. Protection measures originally provided were no longer in use. The equipment had not been maintained and the operators were not familiar with the procedures.
- Inadequate on-line alarmed instrumentation: very little of the required fundamental instrumentation was provided and not all analyzer readings were sent to the plant distributed control system (DCS) and alarmed in the control room. (See <u>Table 4</u> for further details. The entries underlined designate the missing instrumentation at this plant compared to the required fundamental level).
- Not challenging the cycle chemistry status quo: the feedwater and boiler water treatments and control limits were not optimal. Specification of chemical treatments was largely determined by the chemical supplier and plant personnel were not fully aware of the active chemical composition of the products they were feeding.
- No Action Plans for any of the above repeat situations: very often because the plant staff had accepted these situations as "normal and allowable" under the culture, but in other cases they were ignored for various reasons.

The cycle chemistry culture of this plant was no longer sustainable once the boiler was modified to reduce stack emissions. This triggering event with no apparent direct ties to cycle chemistry moved the operation of this unit from acceptable (though very clearly deficient) to unacceptable in the eyes of the organization. The high levels of corrosion products (exacerbated by high air in-leakage and the absence of effective shutdown protection measures) transported to the boiler began to deposit at different locations and to accumulate quickly to levels at which contamination previously tolerated was now sufficient to cause hydrogen damage and lead to localized short term overheating and creep damage. Chemical cleaning practices were no longer sufficient to remove the deposits in time to prevent this damage. The instrumentation was incapable of alerting the operators, who were ill-prepared to respond to chemistry excursion events. Deficiencies in the chemical treatment approach and their contributions to the damage were not understood and once the damage began, the plant continued to operate in exactly the same way.

The final action plan recommended to prevent further failures by hydrogen damage in this unit included several cycle chemistry items, which are summarized as follows.

- Feedwater treatment optimization to reduce corrosion product transport to boiler:
 - Change treatments and limits.
 - Control dissolved oxygen in the condensate; reduce air in-leakage.
 - Monitor iron and copper to optimize treatment.
- Boiler water treatment optimization:
 - Use a phosphate treatment employing tri-sodium phosphate only (or caustic treatment as the boiler pressure allows this option).
- Install needed fundamental analyzers, and have them connected to, and alarmed in, the control room.
- Collect waterwall tube samples during maintenance outages; chemically clean as needed to prevent damage at higher deposit levels.

Parameter	Sample Location
Cation conductivity	CPD, EI, BD, SS or MS or RH
Specific conductivity	Makeup, BD
рН	EI, BD
Sodium	CPD, SS or MS or RH
Dissolved oxygen	<u>CPD, El</u>
Phosphate	BD
Oxidation-reduction potential (ORP)	DAI

Table 4:

Water chemistry analyzer assessment results for the unit in Case Study 2. The entries underlined designate the missing instrumentation at this plant compared to the fundamental level of instrumentation required.

Notes:

- CPD condensate pump discharge, EI economizer inlet, BD blowdown, SS saturated steam, MS main steam, RH – reheat steam, DAI – deaerator inlet.
- 2) Air in-leakage should be monitored on a daily basis.
- 3) Drum carryover should be conducted semi-annually [3].
- 4) Main steam or (hot) reheat steam preferred over saturated steam.

- Improve condenser leak control.
- Develop and implement unit shutdown and layup procedures.
- Provide plant operator cycle chemistry training.

The owner is now considering the means by which the action plan can be implemented.

By inspection, it can readily be seen that nearly all of the repeat situations discussed earlier were in existence at this plant prior to the hydrogen damage failures and performance of the root cause analysis. Thus it has been at risk of damage for many years and will continue to be as long as the situations are not corrected.

Case Study 3: Triple Pressure Combined Cycle Unit Assessment

Case Study 3 is different from the first two in that it reflects the findings of a proactive assessment of the cycle chemistry requested by the owner along with a preliminary assessment of thermal fatigue susceptibility in a relatively new two-on-one combined cycle unit that has not experienced any damage during the first few years of service. The plant at which this unit is located is owned and operated by an independent power producer organization. The review activity was requested as a means of ensuring long range protection of the asset and was requested by the management.

Assessment of the cycle chemistry program by the authors entailed several tasks, including benchmarking of the chemistry program, evaluating the condition of waterside surfaces of the low, intermediate and high pressure evaporators, investigating cycle susceptibility to flow-accelerated corrosion (FAC), internal inspection of the ACC, and development of an action plan designed to address program deficiencies and improve the chemistry program.

It is interesting to note that although this plant received a benchmark rating on a worldwide basis in the "above average" range (mainly by virtue of the short time in service) there were several aspects of the program that were already developing into repeat situations that would, if accepted as part of the plant culture, lead to future damage and failure incidents.

In performing the assessment it was clear that a number of repeat situations were already active, while others were inferred to exist. Known repeat situations included use of non-optimized feedwater and boiler water treatments, condenser air in-leakage at levels sufficient to raise dissolved oxygen in the feedwater above $10 \ \mu g \cdot kg^{-1}$, the absence of satisfactory shutdown protection measures, and instrumentation deficiencies. These situations suggest that elevated levels of corrosion products in the feedwater and subsequent formation of high levels of waterside deposit

may be present. However there was insufficient analytical data on iron transport to verify this. The latter repeat situation, if confirmed, will be exacerbated by the fact that the HRSGs have never been chemically cleaned. Also, no tube samples had been removed from the high pressure evaporator to appraise deposition characteristics. Internal inspection findings confirmed that the feedwater chemistry is not optimized and will, in the absence of action, lead to damage and component failures later in life. For example, photographs confirmed that the interior surfaces of the low pressure steam drum were red, reflecting the high dissolved oxygen concentrations present as a result of air inleakage, even with the unnecessary use of a reducing agent.

Key elements of the action plan for improvement of the chemistry program to prevent the repeat situations leading to failure/damage were as follows:

- Collection of tube specimens from the high pressure evaporator of each HRSG so as to have an indication of the risk of future damage by underdeposit corrosion or overheating mechanisms and to permit chemical and metallurgical analysis of deposits.
- Placement of added emphasis on iron monitoring as a means of assessing the effectiveness of the feedwater treatment program.
- Inspection of the low pressure evaporators for possible FAC damage.
- Improve control of cycle air in-leakage so as to control dissolved oxygen in the feedwater.
 - Take control of the cycle chemistry program, which was being administered by the chemical supplier. (This action is essential to challenge and change the status quo.) Know what active chemicals were included in each product.
 - Terminate use of reducing agent to eliminate damage by single-phase FAC.
 - Ensure that solids-based evaporator treatments contain no acid phosphate compounds; as the condenser is air-cooled, conversion to all-volatile treatment (AVT) could also be considered.
 - Evaluate effect of feedwater treatment on ACC corrosion activity and condensate iron levels.
 - Match allowable steam cation conductivity limits to treatment used.
- Establishment of effective unit shutdown and layup procedures to address early observation of pitting and tubercles.
- Upgrading of the on-line water chemistry analyzers to the fundamental level with concentration on adding cation conductivity and dissolved oxygen analyzers and directing all chemistry analyzer readings to the DCS with alarms in the control.

This organization has avoided development of yet another repeat situation by questioning the chemistry program status quo at the plant. The Action Plan developed should, if followed by the plant with the support of the management and cooperation of the chemical supplier, avoid damage events that would have inevitably developed.

Case Study 4: FAC Assessment

Several organizations have begun to refresh their FAC programs for various reasons. In many instances programs have only received limited attention for several years and there have been staffing changes in the organization. There are many organizations where there has been little if any attention paid to FAC and the organization is essentially starting from ground zero.

Many fossil FAC programs fail to consider the cycle chemistry even though it has direct bearing on susceptibility to single-phase FAC damage. Comprehensive FAC programs consider the influence of the feedwater chemistry in addition to inspection of the piping for evidence of wall thinning. Failure to do this can result in misdirection of available inspection resources. This often becomes a repeat chemistry situation specific to FAC susceptibility. Important aspects of this repeat situation are often applicable to specific fossil plants as follows:

- The feedwater chemistry is not properly matched with the feedwater metallurgy and unit design. It is particularly difficult when changing copper feedwater heaters to stainless steel.
- Iron testing is not effectively used as a means of determining the existence of FAC and identifying components where FAC is active. (This requires proper selection and prior optimization of the feedwater treatment. The minimum levels of iron achievable in the feedwater are dependent on the feedwater treatment applied; higher levels, in the absence of deficiencies in treatment optimization, generally indicate active FAC.)
- Reducing feedwater treatments are used in units with all-ferrous feedwater metallurgy; exclusive use of stainless steel feedwater heaters substantially increases susceptibility to single-phase FAC damage when the cycle is treated with a reducing agent.
- Units with reducing feedwater are allowed to operate with low levels of dissolved oxygen (< 1 μg · kg⁻¹) thereby allowing the reducing environment to dissolve the protective magnetite layer at locations of high turbulence.
- Acceptance of the negative impact of increased iron transport on boiler/evaporator deposition activity, thus requiring more frequent maintenance cleaning or increasing the risk of tube damage by underdeposit corrosion.

In contrast to the combined cycle fleet (as discussed in Case Study 3), the conventional fossil industry has pretty well accepted the fact that the oxidizing feedwater treatment (OT) chemistries are best suited to fossil units with all-ferrous metallurgy. While this approach is clearly best for single-phase FAC, conventional fossil units remain vulnerable to two-phase FAC at locations where two-phase flow exists. Optimization of the feedwater treatment has been shown to be of some benefit but cannot completely protect the surfaces subject to two-phase fluid conditions during unit operation.

In Case Study 4, the cycle chemistry was considered as part of a larger project to assess the FAC susceptibility of a fossil plant with several units with once-through boilers and all-ferrous feedwater metallurgy. It should be noted that the plant acted in response to a number of failures of large-diameter piping including some in locations not widely recognized as possible FAC locations. The FAC review effort revealed a variety of chemistry program deficiencies (repeat situations), many of which had bearing on the susceptibility to two-phase FAC damage. Included here was the fact that the venting of the feedwater heaters and deaerator continued, resulting in low pH in the twophase regions. Also in order to maintain some oxidizing capacity in the moisture component of two-phase fluids, it is desirable to keep these vents closed. In addition, the units were missing many of the fundamental analyzers needed for effective OT monitoring and control. There was only limited provision to confirm supplemental monitoring of iron prior to the condensate polishers or in the feedwater to the boilers as is useful in assessing feedwater treatment effectiveness. Not knowing whether the iron levels at the economizer inlet exceed $1 \ \mu g \cdot kg^{-1}$ in a supercritical unit is a clear repeat situation. But more importantly not knowing the iron levels in the drains provided no indicator of whether there might be two-phase FAC in these systems.

Although the focus of this effort was on the FAC program, consideration of the influence of the cycle chemistry confirmed that a number of repeat situations existed. The plant instrumentation was not fully matched to the demands of an OT chemistry program and supplemental iron testing was not practiced. Shutdown protection systems were not operable, though rarely needed, as the units at this plant were generally in operation. These situations, plus a less than optimal adaptation of the OT chemistry, likely resulted in higher than optimal levels of corrosion product transport. The condensate polishers captured some of this iron; however, the net effect of these practices on deposition in the boilers was beyond the scope of work.

As is so often observed, failure to challenge the chemistry program status quo was perhaps the most serious of the repeat situations noted, with connection to all of the other items. Allowing the other repeat situations to continue without action certainly appears to have had some direct effect on the damage and failures by two-phase FAC in units in this plant.

PROACTIVE PHILOSOPHY AND APPROACH FOR CYCLE CHEMISTRY IN CONVENTIONAL AND COMBINED CYCLE PLANTS

For well over 25 years the optimum way to approach BTF, HTF and CCI has been to adopt management-supported, multi-disciplinary, coordinated programs which are mandated by, and fully supported from, the executive level through a corporate directive or philosophy [4]. These programs have a proven track record of continuous success. However, most recently (3–5 years) in the markedly changing power plant environment it has been recognized that the emphasis of some of these programs has reverted to an "availability loss" program where the current year equivalent availability becomes the dominant parameter or index. This approach moves the organization away from conducting root cause assessments and evaluating the overall damage (thus setting a path to future repeat failures).

In parallel to this movement by the industry the whole concept of repeat situations has emerged as being the most important factor of relevance in recognizing vulnerability to cycle chemistry-influenced damage. In consideration of this, a revision of the historical BTF/HTF/CCI approach has been developed which should avoid these pitfalls by incorporating repeat cycle chemistry situations into the goals of the plant management. To accomplish this, the executive level inserts an expanded set of goals for each plant into the corporate directive for BTFR, HTFR and CCI which includes defining the repeat situations which exist in the plant and includes provisions that require the plant to develop action plans to address them. Quite simply, the message on the cycle chemistry side is that the existing repeat situations are unacceptable and cannot be allowed to continue. From the list of ten repeat situations, a plant may often recognize that multiple repeat situations apply, thus increasing their degree of risk. The action plan developed under the corporate mandate should thus give consideration to the priority for actions as well as the overall timeline and resource requirements required to implement them.

DEVELOPMENT OF THE FIRST REVISION TO THE CYCLE CHEMISTRY BENCHMARKING PROCESS

In 2000 the concept of benchmarking cycle chemistry programs was introduced [5]. Subsequently this process has been applied in its original form to well over a 100 organizations/plants/units worldwide. It has become the arbiter by which plants can compare themselves on a worldwide basis. Similar processes were also developed for boiler tube failures, HRSG dependability and FAC. It is now time to make the first revision to this process for cycle chemistry. The authors have introduced a factor which questions the number of active repeat situations in a plant/system. The factor needs to be non-subjective to fit with the other factors. The new process needs to be tested in plants at a number of organizations prior to publication. The findings will be discussed in a future paper.

CONCLUSION

In assessing the mechanism of damage and root causes associated with cycle chemistry-related damage events, the presence of several repeat situations that have not been corrected is the common denominator. Sometimes individual situations are longstanding with no apparent detriment. However, the development of additional repeat situations or making operational changes to the cycle that may not be perceived as related to the cycle chemistry often serve as triggers for the damage. Increased emphasis on near term availability, often to the detriment of a proper damage assessment, invites additional future damage via continuation of the existing repeat situations. Reversing this trend is only possible by adaption of proactive programmatic strategies that recognize the negative impact of repeat situations and create incentives to correct them in a timely manner.

Finally it appears clear that these repeat situations relate to the basics of power plant chemistry, but most have been degraded as key aspects of continuing cycle chemistry programs. Very often an organization will know to adhere to guideline limits for cation conductivity, pH, sodium, etc. Some organizations even go further and develop a series of compiled or accumulative indicators ("boiler index," "steam index") but do not address the repeat situations. Only addressing the former is now known to represent a totally inadequate approach in many instances. Confidence in such indices by the management/executives often results in failure/damage in the plant/unit with the best indices!

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