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Water quality and monitoring requirements for paper mill boilers operating with high purity feedwater

Scope

High paper mill boiler operating steam pressures require careful examination of water quality control limits and monitoring procedures to assure maximum system reliability. The guidelines applicable to water treatment programs for modern paper mill boiler systems are provided and explained. The monitoring and sampling procedures and sampling methods necessary for such operating conditions are detailed.

This paper deals with water quality and monitoring requirements. It is important to take the appropriate corrective action whenever these requirements are not being met. To that end, the Water Treatment Subcommittee of the TAPPI Steam and Power committee has published TIP 0416-05, “Response to Contamination of High Purity Boiler Feedwater.” Mills that experience feedwater contamination should adopt its recommendations.

Safety precautions

Safety precautions should be followed when sampling high pressure and/or high temperature water and steam. When sampling steam or hot water, it is necessary to use a properly operating sample cooler to prevent injuries from burns. In addition, the use of a properly operating sample cooler will preserve the integrity of the sample.

Definitions

Feedwater is the water fed to the boiler for the purpose of generating steam.

Condensate is the pure water resulting from the condensation of steam into water that is used as part of the feedwater going to the boiler.

Makeup is the treated water that is used to replace the water lost from the boiler as blowdown as well as the steam and condensate that is lost from the system.

Attemperating water is water that is sprayed into superheated steam for the purpose of controlling the temperature of the steam.

Content

Substantial increases in energy costs during the past decades have accelerated the trend toward higher boiler steam operating pressures in the paper industry. Operation at pressures above 6,205 kPa (900 psig) requires significantly improved makeup and condensate quality, more stringent control of boiler water chemistry and steam purity and more sophisticated and comprehensive monitoring techniques and equipment. For convenience, many mills use the high purity feedwater for both the high pressure and low pressure boilers. While this paper addresses only the high pressure boilers, the proper control and monitoring of the low pressure boilers should not be overlooked. The purpose of this paper is to offer water quality guidelines and control limits and to suggest sample

point locations, collection methods and analytical procedures for the guidance of those responsible for designing and operating high pressure steam generating equipment for the paper industry.

The paper emphasizes discussions of feedwater, boiler water and steam purity. It further defines the required monitoring parameters and sampling points to define recommended water quality. The scope of this paper does not permit detailed discussion or recommendations concerning the types of makeup water or condensate treatment processes required to meet the suggested limits. The intent is to indicate the feedwater, boiler water and steam purity necessary to control the usual boiler system waterside problems - corrosion, deposition and carryover - to assure system reliability.

This information should be of special importance to those involved in designing new plants as well as those responsible for improving operation of existing high pressure paper mill boiler systems. Design engineers and others examining equipment options for new systems must be aware that long-term reliability requires water treatment equipment designed with sufficient flexibility to handle deviations from normal operating conditions. Raw water characteristics and operating conditions for individual systems require the use of engineering judgment during design for appropriate process and equipment selection.

Although specific recommendations for methods of external treatment are not within the scope of this paper, it should be noted that meeting the requirements set forth will usually require dual bed/mixed bed demineralizer or reverse osmosis/mixed bed demineralizer quality makeup water. Furthermore, meeting the condensate quality specifications will usually require some type of polishing process. Boilers operating below 6,205 kPa (900 psig) generally do not require this high purity feedwater and may have makeup water systems that consist of zeolite softened, reverse osmosis/zeolite softened water or dual bed demineralizer water as the makeup quality. However, this paper will be concerned only with the use of high purity makeup water.

Sampling points

The recommended sampling points are shown in Figure 1, a flow diagram of a typical high pressure paper mill system. Both continuous and manual (grab) sampling points are designated. The purpose of the manual sampling points is to allow for supplemental sampling and analysis in the event of system upsets involving water treatment and to check the operation of the automatic analyzing equipment. While testing methods are identified, no attempt has been made to specify test methods unless only one particular method has proven to be clearly superior to other methods available. Otherwise, any suitable test method of sufficient *accuracy* may be selected as preferred by the operating personnel. **CAUTION:** Properly designed sample coolers should be used when sampling high temperature water and steam. Properly cooled samples are necessary for both personnel safety and analytical accuracy.

Limits

The expected and maximum limits for all recommended continuous sampling points, are shown in Table 1. The expected limits are those which should be readily maintained in day-to-day operation. Maximum limits are those which cannot be exceeded without incurring unacceptable risks. Where possible, the potential problems resulting from exceeding the maximum limits, either on a short or long term basis, are explained. In the interest of providing maximum system reliability, the limits proposed are conservative and apply to high pressure systems in general. After careful consideration of an individual boiler system, more or less conservative limits specific to that system may be selected.

The importance of maintaining control factors consistently within limits cannot be over emphasized. Paper mill utility management personnel must continuously stress this point with operators and must maintain and continually examine water treatment control records to be certain that prompt and correct actions are being taken when deviations occur. The cumulative effect of even minor deviations, frequently repeated, can eventually lead to serious problems.

Feedwater

For the majority of paper mill boiler systems operating on high purity feedwater, the feedwater consists of treated makeup, combined condensate, deaerating heater steam and any added treatment chemicals. Some high pressure paper mill boiler systems, to avoid the possibility of introducing contaminants to the high pressure feedwater, return mill-wide condensate which is prone to contamination to low pressure boilers while returning

turbine and other clean condensate to the high pressure boilers. Where feasible, this is usually the preferred procedure. The following discussion, however, considers the most typical case in which all the available condensate is present in the feedwater with the feedwater going to both high pressure and low pressure boilers.

The sampling points (shown in Figure 1) required to fully characterize the feedwater are:

1. External makeup from pretreatment
2. Makeup water storage outlet
3. Blowdown/makeup heat exchanger effluent
4. Individual and combined condensates
5. Deaerating heater steam
6. Deaerating heater storage outlet
7. Feedwater after feedwater pump(s)
8. Economizer inlet
9. Economizer outlet

Of these sample points, only Nos. 1, 4 and 8 normally need to be set up for continuous sampling. The other sampling locations are generally used as manual sampling points for one or more of the following reasons:

1. Checking analytical results for the samples obtained at the continuous sampling points.
2. Determining source of feedwater contamination.
3. Backup sample point in the event flow at the continuous sample point is interrupted.
4. Monitoring corrosion and corrosion product migration throughout the feedwater system.

In establishing test parameters and control limits for feedwater, the primary objectives are to protect the boiler and to produce steam of purity suitable for power generation in a turbo-generator. More specifically, the feedwater should be of sufficient purity to minimize formation of deposits, corrosion of metal or carryover of corrosive or deposit forming species in the steam. Feedwater quality requirements for systems operating on high purity water are generally boiler pressure dependent. Specific characteristics of the individual systems must be considered. One case where stringent limits should be carefully considered would be where feedwater is the primary source of water used for spray attenuation or desuperheating. Table 1 summarizes general feedwater quality and testing requirements.

The use of continuous analyzers is suggested for selected parameters. Continuous instrumentation provides around-the-clock coverage of critical parameters and will alert the operator if values stray out of limits. Since any damage due to operation during out-of-limits conditions is cumulative, the time of such operation must be minimized and, therefore, continuous analysis is considered essential.

This equipment should receive maintenance and be calibrated at regular intervals in accordance with manufacturer's specifications. Bench tests should be conducted at regular intervals on parameters monitored by continuous analyzers as a quality control check on instrument performance.

Total hardness

Feedwater should contain no measurable calcium or magnesium hardness since these species can form insulating deposits in boiler tubes. Hardness scales such as calcium sulfate $[\text{CaSO}_4]$, calcium silicate $[\text{CaSiO}_3]$, magnesium silicate $[\text{MgSiO}_3]$ and calcium phosphate $[\text{Ca}_3(\text{PO}_4)_2]$ impede heat transfer in boiler tubes and may eventually cause tube failures due to overheating. In addition, hardness intrusion into a boiler feedwater system operating on high purity water and on coordinated pH/phosphate chemistry can result in a significant depression in the boiler water pH.

Hardness may enter the feedwater either in the makeup or in one or more of the condensate streams. Hardness in the makeup generally occurs due to malfunction of external treatment equipment. Contamination of condensate with hardness may be due to process water intrusion or cooling water leakage into condensate returns from heat exchangers or condensers. When contamination is suspected, samples of makeup water and of each condensate source should be analyzed to determine the cause. Quick action in such circumstances will avoid excessive condensate dumping.

Sodium

Sodium concentrations must be minimized throughout the cycle both to eliminate interference with boiler water alkalinity control and to minimize the presence of sodium in the steam as a result of carryover. High sodium levels in feedwater and, subsequently, in the steam can damage the turbine in two ways. One is by formation of deposits which, if excessive, can result in increased maintenance and reduced turbine efficiency and availability. Another is that sodium hydroxide, sodium chloride or sodium sulfide can cause stress corrosion cracking of the turbine components. High sodium alkalinity may also cause attack on the boiler metal.

Excessive concentrations of sodium in the feedwater may result from contamination of the makeup supply or condensate sources. Indications of high feedwater sodium with other parameters at normal levels suggest sodium leakage from either a makeup demineralizer or a condensate polisher (for systems which include these types of ion exchange equipment).

Silica

Control of feedwater silica concentrations is required for protection of the boiler and turbine. Silica deposits in the boiler can cause tube failures as a result of overheating. Analcite and acmite are especially hard and insulating silica-based boiler scales which can form in the presence of aluminum and iron, respectively. These types of deposits are extremely difficult to remove.

Carryover of silica in the steam due to volatilization may lead to deposition on the turbine blades and reduced turbine efficiency. Specific guidelines for maximum permissible levels of silica can be found in the discussion concerning boiler water, Table 1 and Figure 2.

Silica can enter the feedwater in either the system makeup or the combined condensate. Appropriate makeup and condensate samples should be checked for silica in the event high levels are present in the feedwater. Silica can leak from makeup anion units or enter the system in process contamination.

Iron and copper

The presence of these metals in the feedwater above recommended concentrations (Table 1) usually indicates excessive corrosion rates in the condensate or feedwater areas of the system. Excessive iron in feedwater is commonly caused by iron oxide exfoliation during paper machine start-up cycles. It is a common practice to dump machine condensate until iron levels in the condensate return have reached a low, stable value. Iron and copper may enter the feedwater with system makeup supply but this is a less likely source of contamination.

Feedwater iron and copper are transported to the boiler where they may form deposits. In high purity systems where feedwater hardness levels are normally in the ppb range, iron deposition becomes increasingly troublesome. When porous iron or copper deposits form, they may allow under-deposit corrosion. It has become the standard practice to supplement phosphate/pH control with polymeric dispersants which have proven ability to disperse particulate iron returned in the condensate. These polymers also disperse hardness and other depositables which may enter the boiler as contaminants or due to occasional deviations from normal external treatment control.

Iron and copper may also be present in the saturated steam as a result of carryover or in the superheated steam as a result of iron and/or copper contamination of the attemperating water. Iron may also be present in superheated steam from the exfoliation of iron oxide from the superheater during thermal transients. Iron and copper in the steam can foul valves and form turbine deposits. Iron in the steam often causes solid particle erosion of the first stage turbine blades.

Total organic carbon

No contamination of the feedwater by extraneous organic material such as black liquor or oil should be permitted. In some cases organics may break down at boiler operating conditions to form organic acids or organic based boiler deposits. This is of increasing concern as the boiler pressure rises above 6,205 kPa (900 psig). Furthermore, the organics can carry over in the steam where they may either contribute to corrosion or form deposits in the turbine. The makeup water supply is the most likely source of organics in the feedwater. However, organic contamination of the condensate returns can occur due to black liquor or other process water contamination.

Dissolved oxygen

Dissolved oxygen must be controlled throughout the cycle. Some corrosion mechanisms require the presence of oxygen and most are accelerated by it. High dissolved oxygen concentrations in the feedwater result in more rapid corrosion of metals in the system. Pitting attack in economizers is often associated with high dissolved oxygen levels in the feedwater. Increased corrosion resulting from high oxygen concentrations generates higher concentrations of iron and/or copper in the cycle water.

Dissolved oxygen enters cycle water as the result of air in-leakage in areas of the condensate and feedwater systems which are at low pressure or under vacuum. Pump gland seal water is a relatively common potential source of oxygen contamination. While some air in-leakage is unavoidable, checking for air in-leakage into the cycle is a valuable preventative maintenance activity which should be performed on a regular basis.

Even though a properly designed and operated deaerating heater will remove most of the dissolved oxygen, chemical treatment must be applied to further reduce feedwater oxygen concentration and to guard against deaerator upsets. Historically, sodium sulfite (for low pressure systems) and hydrazine (for high pressure systems) have been applied as oxygen scavengers. More recently, proprietary hydrazine substitutes have been developed for use in applications where concern over use and handling of hydrazine exists. Oxygen scavenger concentration requirements vary both with the particular chemical used and the specific steam generating system; the reaction time for oxygen scavenger to react with oxygen is limited. Control procedures for oxygen scavengers should be as recommended by the chemical consultant.

It should be noted that sulfite is not normally recommended as an oxygen scavenger in units operating at pressures greater than 6,205 kPa (900 psig) because sulfite can decompose to sulfur dioxide (SO₂) and hydrogen sulfide (H₂S) gasses. These gasses become corrosive as the steam condenses in the condensate system. Sulfite should not be used where boiler feedwater is used for steam attemperation or desuperheating.

The problems caused by the presence of any significant quantity of dissolved oxygen in the feedwater can be so serious that, in addition to close observance of the control procedures recommended by the chemical consultant, continuous oxygen testing is recommended as shown in Table I. Should high concentrations of dissolved oxygen in the feedwater be detected, the following steps should be taken:

1. The accuracy of the continuous oxygen analyzer should be determined.
2. The oxygen scavenger feed rate and feed system should be checked.
3. The operation of the deaerating heater should be reviewed.
4. The system should be examined for sources of excessive in-leakage of air or oxygen-laden water.

Long-term operation with feedwater dissolved oxygen concentrations above 10 ppb should not be permitted.

The preferred sample point for measuring dissolved oxygen is after the boiler feedwater pump discharge in order to detect oxygen intrusion through the boiler feedwater pump(s), such as a leak in the cooling gland or an air leak on the suction side flange on the pump.

pH

Proper control of feedwater pH is necessary to minimize corrosion, reducing both metal wastage and feedwater corrosion product contaminants. It has also been recommended by NACE that feedwater pH be maintained at 9.0 units or above to mitigate the potential for environmentally assisted cracking of the weld and heat affected zones of the deaerating heater and storage tank. The pH should not exceed 9.2 pH units if copper alloys are present in the system.

Excursions in feedwater pH may be indicative of contamination by either alkaline or acidic species including sodium, silica, organics, chlorides and sulfates. Manual testing should be initiated to identify the source of the contamination.

Monitoring for pH, at least on a periodic basis, throughout the entire condensate system is essential not only to avoid serious pH deviations but also to assure proper distribution of the neutralizing amine employed for the purpose of minimizing both corrosion and corrosion product pickup in the system.

Specific conductivity

Specific conductivity is a measure of overall water purity. High specific conductivity readings in the feedwater indicate contamination. Deviations in feedwater conductivity may be noted before limits are exceeded for other control parameters. The specific contaminant(s) responsible for increased conductivity and the source of contamination should be identified and necessary corrections made as soon as possible. ***Continued long-term operation with high specific conductivity in the feedwater will lead to operating problems.***

Boiler water

As shown in Figure 1, continuous boiler blowdown (Sample Point Location #10) is the proper location for surveillance of boiler water quality. Suggested control limits for boiler water are included in Table 1.

The boiler water treatment method selected should be designed to provide maximum protection against corrosion, deposition, carryover, and silica vaporization. Control of carryover and silica vaporization is accomplished by maintaining boiler water dissolved solids (as indicated by conductivity) and silica levels within specified limits. Prevention of corrosion and deposition can be accomplished by several approaches involving different types of internal treatment chemicals. Those most commonly employed are phosphates, caustic soda, and polymeric dispersants. Alkalinity or pH control limits are necessary to assure maintenance of the proper boiler water chemistry. Control of the internal treatment chemicals will require boiler water tests such as alkalinity, phosphate and pH. The parameters and limits for a particular system should be determined by means of consultation with the chemical supplier or water treatment adviser.

Silica

Except during mill startup, excessive silica concentrations in the boiler water occur only rarely. With properly operated demineralizers, the level of silica in the boiler water is usually maintained below the guidelines established in Figure 2. However, colloidal (non-reactive) silica, present in some makeup supplies, can pass through the anion unit of the demineralizer to contaminate the feedwater and, subsequently, the boiler water. Under boiler conditions, the colloidal silica is rapidly converted to reactive silica and can potentially form waterside deposits. Colloidal silica is particularly troublesome in surface waters following periods of heavy runoff as a result of rainfall or melting snow.

Because silica volatility increases with temperature, high concentrations of silica in high pressure boiler water can result in turbine deposits which can reduce output and turbine reliability. Turbine manufacturers continue to reduce the maximum silica level recommended in the steam. Consultation with the turbine manufacturer and the silica curves shown in Figure 2 should be used to determine the maximum permissible boiler water silica concentration for a particular system.

Conductivity

Conductivity measurement provides an indication of the concentration of dissolved solids in the boiler water. Conductivity levels in excess of control limit values may indicate either contamination of the feedwater or improper control of internal treatment chemicals. Either of these conditions increases the risk of deposition or corrosion in the boiler and carryover in the steam. Additional samples should be analyzed, as necessary, to identify the source of boiler water contamination. Boiler blowdown rates should be increased as necessary to maintain conductivity levels within limits as specified in Table 1 or through consultation with a water treatment specialist.

Alkalinity/pH/Phosphate

Control of boiler water pH can be troublesome. Higher than anticipated pH has been traced to sodium leaking through the cation exchange resin or being slowly released by fouled and/or degrading anion resins. Sodium leakage can also be due to the presence of cation resin in the anion bed. Since sodium leakage can result in high sodium hydroxide levels in the boiler, monitoring of the treatment makeup for sodium is recommended in Table 1.