Guidelines for properly sampling steam & condensate in Yankee dryer steam systems

Scope

This Technical Information Paper (TIP) provides guidelines on the safe and effective testing of paper machine steam and condensate water quality in order to prevent problems and equipment damage.

Definitions

Black Oxide = A form of Iron oxide called Magnetite (Fe₃O₄),
Red Oxide = A form of Iron oxide called Hematite sometimes spelled as hematite, is the mineral form of iron(III) oxide (Fe₂O₃), one of several iron oxides. Commonly known as “red rust”.

Safety precautions

Operations, maintenance, and inspectors to follow OSHA or Local standards as well as safe sampling guidelines as defined in NB Technical Paper entitled “Preventing Steam/Condensate System Accidents”. Steam and or water pressure to be relieved and proper lockout tagout procedures to be followed prior to repairs.

All personnel shall use the specified personnel protective equipment (PPE). Recommended PPE is:
- Leather gloves
- Safety eyewear
- Hearing protection
- Long sleeves
- Steel toed shoes

Introduction

Sampling condensate streams correctly can be very challenging. There are many ways to do it incorrectly and deliver incorrect results. If these results are used to make operational or chemical decisions around the Yankee then damage to the unit could result. These recommendations come from TAPPI, ASME and EPRI guidelines.

In the tissue manufacturing process, the performance of the Yankee dryer has a direct impact on the quality of the finished product. Yankee dryer performance is directly related to the continuous delivery of a high quality steam supply to the dryer and an efficient evacuation system to remove the condensed steam. Both of these elements are critical in maintaining a consistent skin temperature across the dryer surface. These key elements are influenced by the operation of the boiler pretreatment system and control / monitoring of the return condensate chemical treatment program.
When the Yankee dryer performance declines, the tissue machine may experience reduced drying capacity, increased pressure drop at constant steam blowthrough, wet streaks and random coating patchiness. Eventually the crepe quality and uniformity of the sheet will degrade and chatter can occur. When these symptoms become apparent, it is too late, quality and production have already been adversely affected!

The root cause of poor performance internal to the Yankee Dryer is the pluggage of soda straws. The principal component of the deposit is usually iron in the form of magnetite (Fe₃O₄). The black magnetite is generated by the corrosion of the Yankee shell and condensate piping due primarily to exposure to carbonic acid. The carbonic acid is produced by the breakdown of alkalinity in the boiler water. The alkalinity is present due to waters ability to dissolve almost everything it comes in contact with. Limestone and dolomite make up much of the aquifers in the Midwest. Limestone (CaCO₃) and dolomite (MgCO₃) dissolve in the groundwater. The cations in this reaction, calcium and magnesium, are removed by the sodium zeolite softeners, but the alkalinity portion is not removed by simply softening the water because the alkalinity is anionic. As most tissue mills operate low pressure boilers they usually operate only softening systems that only remove cations and not the more complicated demineralizer systems which will remove nearly 100% of the dissolved cations and anions in the boiler feedwater.

Steam / Condensate Chemistry – Effect of Alkalinity and Oxygen

As mentioned above the boiler pretreatment system has a direct effect on the amount of carbonic acid and oxygen that can enter the Yankee dryer system and negatively affect its performance. In sodium zeolite softened water systems all of the raw water alkalinity is allowed to enter into the boiler feedwater system. Under boiler water temperature and pressure conditions the alkalinity breaks down and carbon dioxide gas is generated. The reaction is shown below.

$$2\text{HCO}_3^- \xrightarrow{\text{Heat}} \text{CO}_3^{2-} + \text{H}_2\text{O} + \text{CO}_2$$

**Fig. 1:** Breakdown of feedwater alkalinity

The carbon dioxide gas travels out with the steam and possesses no cause for operational concern until the steam is condensed back into a liquid form. At that point, the condensing water reacts with the CO₂ gas forming carbonic acid which will equilibrate in solution as shown by the reaction below.

$$\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3$$

**Fig 2:** Carbon dioxide and steam equilibrium reaction

Systems operating with higher boiler feed water alkalinity will generate more carbonic acid in the return condensate system and, if not continuously monitored and adjusted for, will produce periods of depressed condensate pH and a more corrosive environment to the return condensate internals including the Yankee dryer. It should be noted that the remaining bicarbonate alkalinity will recycle with the return condensate, back to the boiler, where it will once again breakdown to form additional carbon dioxide that will leave with the steam.

Next we must understand a little bit about what it is we are measuring. pH is the negative log of the hydrogen ion concentration in the sample stream. The logarithmic nature of this measurement makes accuracy of testing even more crucial, as every one unit change in pH represents an order of magnitude change in the hydrogen ion concentration.
A pH of 5.5 is 10,000 times more aggressive to mild steel than a pH of 7.5 and 1,000,000 times more aggressive than a pH of 8.5. Since corrosion rates increase with temperature, the aggressiveness of a low pH condensate cannot be ignored. The graph below shows how carbon dioxide can depress the pH of pure water at different temperatures.

![Graph showing pH depression of carbon dioxide at different temperatures](image)

**Fig 3: pH depression of carbon dioxide at different temperatures**

According to Fig. 3, as little as 1 ppm of carbon dioxide can drop the pH to 5.5. Many tissue mills have added reverse osmosis units either in front or behind the sodium zeolite softeners to reduce the alkalinity of the feedwater. A properly operating reverse osmosis unit can be expected to remove 95% or more of the dissolved ionic solids in the boiler water. If the raw water has an alkalinity of 100 ppm then the output of the reverse osmosis unit would still have 5 ppm of alkalinity and as the graph above shows, this can seriously depress the condensate conductivity.

The pH of pure condensate at 140 deg F is 6.5. This explains the observation that Yankee Dryer systems will not experience plugged soda straws if condensed steam sample going into the Yankee has a pH of 6.5, but will often have plugged straws if the pH is 5.5 or below.
Yankee dryer performance is directly related to the effective removal of the condensed steam from within the dryer. A common Yankee dryer condensate removal design utilizes “soda straws” to evacuate the condensed steam. If flow through these straws is restricted, the condensate can build up within the dryer causing inefficient operation and poor sheet quality. The most common cause of soda straw flow restriction is plugging of the straw orifice with iron, usually as a black magnetite deposit. The tip of the soda straw is very susceptible to deposit formation due to the large pressure drop experienced in that section of the pipe. These deposits can be caused by the formation of active corrosion by-products within the dryer system or by the rapid release of the passive magnetite layer which forms on the drum wall and internals. Both of these events can occur when a corrosive atmosphere is present within the Yankee dryer system.

A corrosive atmosphere will be present whenever there is an imbalance between the level of carbonic acid and oxygen present within the condensate stream and the chemical treatment program utilized to neutralize/scavenge these elements. Because of the dynamic nature of the tissue machine operation (grade changes, breaks, etc.) this balance is continuously shifting making it difficult to maintain a non-corrosive atmosphere at all times.

Oxygen can also cause corrosion in Yankee dryers. Oxygen can enter the Yankee through air in leakage or from the boiler system. Oxygen dissolved in 140°F pure condensate is 6% to 10% more corrosive to iron than its carbon dioxide molar equivalent.

When both carbon dioxide and oxygen are present the resulting corrosion rate is 10% to 40% greater than the sum of the corrosion rates of the two gases acting separately.

A critical element effecting Yankee dryer performance and reliability is in the establishment and maintenance of a thin passive layer of iron oxide on the internal drum surfaces referred to as the magnetite layer. Metal passivation is a critical process that occurs and provides protection of the Yankee dryer system. Passivation is the formation of an insoluble nonporous protective oxide on a metal surface. Cast iron and steel will self passivate in water if no contaminants are present. The reaction is very slow under 212°F. Passivation can be accelerated by the use of chemical treatment (amines), however, under the operating conditions present within the Yankee dryer system, the passivated layer is not very robust and is easily damaged, both mechanically and chemically if the system is not properly controlled. Damage to the magnetite layer will release particulate iron into the bulk condensate stream and, depending on severity, cause a threat of plugging at the tips of the Yankee dryer soda straws. The reactions that drive the passivation process are shown below.

1) \( \text{Fe}^0 \rightarrow \text{Fe}^{+2} + 2e^- \) (ionized)
2) \( \text{Fe}^{+2} + 6\text{H}_2\text{O} \rightarrow [\text{Fe(H}_2\text{O})_6]^{+2} \) (hydrated)
3) \( [\text{Fe(H}_2\text{O})_6]^{+2} \rightarrow \text{Fe(OH)}_2 + 2\text{H}^+ + 4\text{H}_2\text{O} \) (hydrolyzed)
4) \( \text{Fe}^{+2}(\text{OH})_2 + 0.5\text{H}_2\text{O} \rightarrow \text{Fe}^{+3}(\text{OH})_3 + 0.5\text{H}_2 \) (oxidation)
5) \( n \text{Fe}^{+3}(\text{OH})_3 \rightarrow [\text{Fe}^{+3}\text{O(OH)}]_n + n \text{H}_2\text{O} \) (polycondensation)
6) \( 2 [\text{Fe}^{+3}\text{O(OH)}]_n + n \text{Fe}^{+2}(\text{OH})_2 \rightarrow n \text{Fe}_3\text{O}_4 \)

**Fig 4:** Passivation process reactions

The base metal of the Yankee dryer can either passivate or corrode. Under passivating conditions the inside of the Yankee Dryer will become black as the iron passivates and forms the protective magnetite layer (Fe$_3$O$_4$). The presence of oxygen will drive the reaction to the corrosion side rather than the passivation side and a red layer will be produced in the Yankee Dryer. This red layer is hematite (Fe$_2$O$_3$). Magnetite is preferred over hematite due to the improved heat transfer of magnetite over hematite. In addition magnetite makes a very dense
nonporous layer while hematite produces a softer and more porous layer that is prone to the formation of under deposit corrosion. Flash corrosion often occurs when a hot Yankee Dryer is opened, especially in humid conditions. The flash corrosion layer can usually be wiped away with a glove, revealing the preferred black magnetite layer below.

**Chemical Treatment**

Two treatment chemistries are important for the proper operation of the Yankee Dryer steam system. Some type of oxygen scavenger must be fed to the deaerator to reduce the dissolved oxygen in the feedwater to zero. Any oxygen that remains in the feedwater and is not chemically scavenged will either corrode the economizer or run up piping to the boiler or flash and go off into the steam system. As mentioned before oxygen and carbon dioxide together produce a much more corrosive condition that either gas by alone. Unless the boiler feedwater is demineralized to remove the alkalinity some carbon dioxide will always be present so we must eliminate the oxygen in these systems.

Neutralizing amines are a family of chemistries that can be used to neutralize the carbonic acid produced steam and condensate systems. Different amines have different vapor to liquid ratios. The vapor to liquid ratio determines how far the amine will travel with the steam. Picking the correct product is very site specific and proper pH measurement of the condensate coming out of the Yankee Dryer is critical to picking the right product or products. In a complicated tissue mill with multiple boilers and Yankee Dryers it is often times necessary to have a small satellite amine feed in front of each Yankee Dryer.

The graph below explains why the pH range of 8.8 to 9.2 is often chosen for condensate systems. Yellow metals, copper, brass and admiralty; have a bath tub shaped corrosion curve. The bottom of that curve is between 8.8 and 9.2. Carbon steel corrosion rates continue to trend downwards at pH increases. Many Yankee Dryers incorporate large copper washers under the bolts so yellow metal protection is usually important to these systems.

![Fig 5: Rates of corrosion at different pH levels](image)

Neutralizing amines are volatile and are usually fed to the steam header or into the feedwater after the deaerator. Because they are volatile they should not be fed prior to the deaerator as much of the product will be lost to the vent. The amines will condense with the steam and combine with the carbonic acid to form an amine carbonate. The amines also have basicity which then elevates the pH of the condensate to the target range of 8.8 to 9.2. The amine carbonate returns with the condensate to the boiler where it breaks back down to amine and carbonate and the cycle repeats. The amine reaction is shown below.
Amine hydrolysis in water:
\[ \text{R-NH}_2 + \text{H}_2\text{O} \rightarrow \text{R-NH}_3^+ + \text{OH}^- \]

Neutral amine water Neutral amine hydroxide

CO₂ hydrolysis in water:
\[ \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{CO}_3 \rightarrow \text{H}^+ + \text{HCO}_3^- \]

Carbon dioxide water Carbonic acid Bicarbonate

**Net reaction:**
\[ \text{R-NH}_2 + \text{H}_2\text{CO}_3 \rightarrow \text{R-NH}_3^+ + \text{HCO}_3^- \]

Neutral Amine Carbonic acid Neutral amine Bicarbonate

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Fig 6: Amine carbonate reaction cycle

**Soluble iron versus Millipore testing**

Many mills will attempt to determine the iron throw from a Yankee Dryer by conducting Millipore tests on the condensate. In order for any particulate iron testing to be accurate the sample flow must be fast enough to carry the heavy iron particles through the sample point. This requires a minimum of 5 feet per second of sample flow. The table below shows the flow requirements for different size sample lines.

<table>
<thead>
<tr>
<th>Line Size (in.)</th>
<th>Wall Thickness (in.)</th>
<th>Sec/ft for init. response @ 500 ml/min</th>
<th>Sec/ft for full response @ 500 ml/min</th>
<th>Flow @ 5 ft/sec (ml/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/4 Tubing</td>
<td>0.035</td>
<td>0.6</td>
<td>1.8</td>
<td>1,501</td>
</tr>
<tr>
<td></td>
<td>0.065</td>
<td>0.27</td>
<td>0.8</td>
<td>667</td>
</tr>
<tr>
<td>3/8 Tubing</td>
<td>0.035</td>
<td>1.72</td>
<td>5.2</td>
<td>4,310</td>
</tr>
<tr>
<td></td>
<td>0.065</td>
<td>1.2</td>
<td>3.6</td>
<td>2,989</td>
</tr>
<tr>
<td>1/2 Tubing</td>
<td>0.035</td>
<td>3.43</td>
<td>10.3</td>
<td>8,567</td>
</tr>
<tr>
<td></td>
<td>0.065</td>
<td>2.5</td>
<td>7.6</td>
<td>6,343</td>
</tr>
<tr>
<td>1 Pipe</td>
<td>Schedule 40</td>
<td>20.4</td>
<td>61.2</td>
<td>50,985</td>
</tr>
</tbody>
</table>

Fig 7: Flow requirements for different size sample lines

The reference slide above shows flow required to maintain iron entrained in sample and purge times for different tube sizes. Data indicates lines larger than 3/8 in tubing are impractical. Tubing smaller than ¼ inch will be prone to plugging. Running a lower flow rates means that some of the iron will deposit in the sample line and give a false low reading for iron throw. If the sample line is opened up beyond normal flow rates the sample will often turn black with the iron that has been deposited in the sample line. A Millipore conducted under these conditions will give false high iron throw data.

Hach has developed a test for soluble iron (Fe²⁺), since the iron is dissolved in the condensate, sample flow rates do not have to be maintained at 5 feet per second. This test is very accurate and delivers good results to the
minimum detection limit of 2 parts per billion. Mills should consider adopting this test as a regular measurement of iron throw from the Yankee Dryer and to optimize the neutralizing amine program.

**Sampling**

For the testing to be accurate, care must be taken to insure a proper sample is obtained and tested in a proper manner. The drawing below shows the recommended sample point installation. The best place to sample the condensate coming out of the Yankee Dryer is the discharge of the Yankee, prior to the condensate collection/flash tank. The sample tap must be in a horizontal section of the line and very close to the bottom, or 6:00 position. The discharge line will contain a two phase flow of steam and condensate. It is critical that only the condensate be sampled to get the best pH measurement. Sampling a mix of steam and condensate will give erroneous results as the carbon dioxide in the steam will condense to carbonic acid and give a potentially false low pH.

[Diagram of sample tap parts and setup]

**Fig 8: Sample tap parts and setup**

**NEVER** attempt to sample hot condensate. The sample must be cooled to less than 25 Deg C (75 deg F) for the sample to be meaningful. The cooling must take place at the sample point. Collecting a sample to a plastic bottle then cooling the bottle in a sink will not yield accurate results. Sampling hot condensate will give erroneous results; it can be falsly high or low.

**NEVER** use a fully condensed steam sample to control the feed of neutralizing amines to the Yankee Dryer. The Yankee Dryer has two phase flow and the Vapor to Liquid ratio of carbon dioxide will put a large amount of carbon dioxide into the vapor phase where it will do no harm to anything. Attempting to elevate the pH of the fully condensed steam sample will result in very high neutralizing amine costs.

Sampling the blowthrough steam is an important test to determine if corrosive conditions exist in the Yankee Dryer. A fully condensed blowthrough steam sample with a pH of 6 and above will usually not be corrosive. A pH below 5 will definitely be corrosive.

**ALWAYS** sample from a continuous sample stream to obtain a representative condensate sample.

**ALWAYS** measure the pH at the sample point. Collecting a sample and carrying it back to the water lab will induce error into the measurement.

**ALWAYS** throttle the sample at the throttle valve, located after the sample cooler.

**ALWAYS** sample with a pH meter dedicated to measuring condensate only. The high concentration of dissolved solids in boiler blowdown makes the pH sample probes inaccurate for the work we need them to do in condensate streams.
ALWAYS place the pH probe at the bottom of the casserole with the sample stream. Condensate will pull carbon dioxide from the air and reduce the accuracy of the measurement.

NEVER stir the sample with the pH probe, this can also pull air into the sample, adding carbon dioxide and reducing the sample accuracy.

ALWAYS use stainless steel to sample condensate. Mild steel cannot be used if any metals testing are going to be done.

ALWAYS maintain a 1.5 meter per second (5 foot per second) sample flow rate when doing any particulate metals testing. The condensate, particulate metals stream is a two phase flow, with solids being suspended in a liquid. If flow rates are not maintained above 1.5 meters per second, solids will drop out of suspension, giving false low numbers.

ALWAYS remember that when both carbon dioxide and oxygen are present the resulting corrosion rate is 10% to 40% greater than the sum of the corrosion rates of the two gases acting separately.

Keywords
Paper machines, Yankee Dryers, Steam, Condensate, Magnetite, Black Oxide, Hematite, Red Oxide

Additional information
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