Water Quality for Supercritical Plants
Objectives and other details of modules

Duration – 75 minutes

Training aids
Power point Presentations

Objective

At the end of the session participants will be able to:

- Explain metallurgical restriction and requirement in supercritical boilers
- Develop capability to take action to maintain chemical parameters
- List out chemical parameters – condensate limits, feed water limits and main steam limits
- Illustrate the process of cycling online chemical instrumentation
- Indicate water chemistry influence on boiler tube failure in supercritical units
- Introduce operators’ best practices relating to water chemistry for supercritical units
What is Supercritical

- As the fluid pressure increases, Latent Heat reduces.
- At critical points it becomes zero.
- In physical terms at this pressure water transforms to steam spontaneously.

Supercritical Parameters:
- Steam Pressure > 221.2 BAR
- Steam Temperature > 374.15°C
Metallurgical restrictions and requirements

- Do not allow for the use of any copper or copper alloys in feed water cycle.

- Copper and copper alloy condensers are acceptable

- 100% full flow deep bed condensate polishing with external regeneration is required
- Cycle chemistry should be oxygenated feedwater treatment.
- Makeup water plant should be capable of producing water with a conductivity of less than 0.1 mmho, with chlorides, sulfates and sodium less than 3 ppb and silica less than 10 ppb.
Chemical Parameters
Action Levels

- **Action Level 1**
  - Parameter is to be returned to normal values within 72 hours. If parameter does not return to normal in 72 hours, parameter moves to Action Level 2.

- **Action Level 2**
  - Parameter is to be returned to normal values within 24 hours. If parameter does not return to normal in 24 hours, parameter moves to Action Level 3.

- **Action Level 3**
  - Parameter is to be returned to normal values within 4 hours. If parameter does not return to normal in 4 hours, a controlled shutdown of the unit shall be initiated.
Abnormal is condition between what is considered normal cycle water chemistry and action level 1.

Operation of unit is limited to two weeks before moving into action level 1 unless an extension is granted.
<table>
<thead>
<tr>
<th>Sample Point</th>
<th>Parameter</th>
<th>Normal Value</th>
<th>Abnormal</th>
<th>Action Level 1</th>
<th>Action Level 2</th>
<th>Action Level 3</th>
<th>Immediate Shutdown of Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Hotwell</td>
<td>Cation Conductivity (mmho)</td>
<td>&lt; 0.20</td>
<td>&gt; 0.20</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>Total Hotwell</td>
<td>Sodium (ppb)</td>
<td>&lt; 3.0</td>
<td>&gt; 3.0</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>Total Hotwell</td>
<td>Dissolved Oxygen (ppb)</td>
<td>&lt; 20</td>
<td>&gt; 20</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>Total Hotwell</td>
<td>Silica (ppb)</td>
<td>&lt; 20</td>
<td>&gt; 20</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>Total Polisher Effluent</td>
<td>Cation Conductivity (mmho)</td>
<td>&lt; 0.10</td>
<td>0.1 – 0.2</td>
<td>&gt; 0.20</td>
<td>&gt; 0.3</td>
<td>&gt; 0.65</td>
<td>NA</td>
</tr>
<tr>
<td>Total Polisher Effluent</td>
<td>Sodium (ppb)</td>
<td>&lt; 3.0</td>
<td>NA</td>
<td>&gt; 3.0</td>
<td>&gt; 6.0</td>
<td>&gt; 12.0</td>
<td>&gt;24.0</td>
</tr>
<tr>
<td>Total Polisher Effluent</td>
<td>Silica (ppb)</td>
<td>&lt; 5.0</td>
<td>&gt; 10</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>Total Polisher Effluent</td>
<td>Sulfate (ppb)</td>
<td>&lt; 3.0</td>
<td>NA</td>
<td>&gt; 3.0</td>
<td>&gt; 6.0</td>
<td>&gt; 12.0</td>
<td>&gt; 24.0</td>
</tr>
<tr>
<td>Total Polisher Effluent</td>
<td>Chloride (ppb)</td>
<td>&lt; 3.0</td>
<td>NA</td>
<td>&gt; 3.0</td>
<td>&gt; 6.0</td>
<td>&gt; 12.0</td>
<td>&gt; 24.0</td>
</tr>
</tbody>
</table>
# Feedwater Limits

<table>
<thead>
<tr>
<th>Sample Point</th>
<th>Parameter</th>
<th>Normal Value</th>
<th>Abnormal</th>
<th>Action Level 1</th>
<th>Action Level 2</th>
<th>Action Level 3</th>
<th>Immediate Shutdown of Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Economizer Inlet</td>
<td>Cation Conductivity (mmho)</td>
<td>&lt; 0.1</td>
<td>0.1 – 0.2</td>
<td>&gt; 0.2 Note 1</td>
<td>&gt; 0.3 Note 2</td>
<td>&gt; 0.65</td>
<td>&gt; 2.0 mmho (5 min.) &gt; 5mmho (2 min.)</td>
</tr>
<tr>
<td>Economizer Inlet</td>
<td>Sodium (ppb)</td>
<td>&lt; 3.0</td>
<td>NA</td>
<td>&gt; 3.0</td>
<td>&gt; 6.0</td>
<td>&gt; 12.0</td>
<td>&gt; 24.0</td>
</tr>
<tr>
<td>Economizer Inlet</td>
<td>Chloride (ppb)</td>
<td>&lt; 3.0</td>
<td>NA</td>
<td>&gt; 3.0</td>
<td>&gt; 6.0</td>
<td>&gt; 12.0</td>
<td>&gt; 24.0</td>
</tr>
<tr>
<td>Economizer Inlet</td>
<td>Iron (ppb)</td>
<td>&lt; 3.0</td>
<td>&gt; 3.0</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>Economizer Inlet</td>
<td>Copper (ppb)</td>
<td>&lt; 3.0</td>
<td>&gt; 3.0</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>Economizer Inlet</td>
<td>Suspended solids (ppb)</td>
<td>&lt; 10.0</td>
<td>10.0 – 35.0</td>
<td>&gt; 35.0</td>
<td>&gt; 50.0</td>
<td>&gt; 100</td>
<td>&gt; 150</td>
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<tr>
<td>Economizer Inlet</td>
<td>pH</td>
<td>8.8 – 9.0</td>
<td>8.1 – 8.8</td>
<td>NA</td>
<td>8.0</td>
<td>7.5</td>
<td>&lt; 7.0</td>
</tr>
<tr>
<td>Economizer Inlet</td>
<td>Silica (ppb)</td>
<td>&lt; 10.0</td>
<td>10.0 – 20.0</td>
<td>&gt; 20.0</td>
<td>&gt; 30.0</td>
<td>&gt; 40.0</td>
<td>&gt; 50.0</td>
</tr>
<tr>
<td>Economizer Inlet</td>
<td>Sulfate (ppb)</td>
<td>&lt; 3.0</td>
<td>NA</td>
<td>&gt; 3.0</td>
<td>&gt; 6.0</td>
<td>&gt; 12.0</td>
<td>&gt; 24.0</td>
</tr>
<tr>
<td>Economizer Inlet</td>
<td>Dissolved Oxygen (ppb)</td>
<td>30 – 150</td>
<td>&lt; 30.0</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
</tbody>
</table>
# Main Steam Limits

<table>
<thead>
<tr>
<th>Sample Point</th>
<th>Parameter</th>
<th>Normal Value</th>
<th>Abnormal Value</th>
<th>Action Level 1</th>
<th>Action Level 12</th>
<th>Action Level 13</th>
<th>Immediate Shutdown of Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Main Steam</td>
<td>Cation Conductivity (mmho)</td>
<td>&lt;0.10</td>
<td>0.10-0.20</td>
<td>&gt;0.20</td>
<td>&gt;0.30</td>
<td>&gt;0.65</td>
<td>&gt;2.0 MMLIQ (5.5 in.) &gt;5 TNRIIH (2 MIN)</td>
</tr>
<tr>
<td>Main Steam</td>
<td>Iron (ppb)</td>
<td>&lt;30</td>
<td>&gt;30</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
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<tr>
<td>Main Steam</td>
<td>Copper (ppb)</td>
<td>&lt;30</td>
<td>&gt;30</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>Main Steam</td>
<td>Sodium (ppb)</td>
<td>&lt;3.0</td>
<td>NA</td>
<td>&gt;3.0</td>
<td>&gt;6.0</td>
<td>&gt;12.0</td>
<td>&gt;24.0</td>
</tr>
<tr>
<td>Main Steam</td>
<td>Silica (ppb)</td>
<td>&lt;10.0</td>
<td>10.0-20.0</td>
<td>&gt;20.0</td>
<td>&gt;30.0</td>
<td>&gt;40.0</td>
<td>&gt;50.0</td>
</tr>
<tr>
<td>MAIN STEAM</td>
<td>Chloride (ppb)</td>
<td>&lt;30</td>
<td>NA</td>
<td>&gt;30</td>
<td>&lt;=5.0</td>
<td>&gt;12.0</td>
<td>&gt;24.0</td>
</tr>
<tr>
<td>Main Steam</td>
<td>Sulfate (ppb)</td>
<td>&lt;30</td>
<td>NA</td>
<td>&gt;10</td>
<td>&gt;6.0</td>
<td>&gt;12.0</td>
<td>&gt;24.0</td>
</tr>
</tbody>
</table>
Cycle On-line Chemical Instrumentation
Cycle Instrumentation

- All chemical instrumentation needs to be alarmed and displayed in the main control room.
- A temperature control unit should be supplied for secondary cooling of the sample lines to ensure cycle samples are maintained at 25°C.
- Hot well cation conductivity mounted locally on each condenser half
- Condensate - cation conductivity, sodium
- Common condensate outlet - sodium, silica, specific conductivity
Cycle Instrumentation

- Deaerator Inlet - Dissolved oxygen
- Deaerator Outlet - Dissolved oxygen
- Economizer Inlet - Cation conductivity, specific conductivity, pH
- Main Steam - Cation conductivity, specific conductivity
- High Pressure Heater Drain - Dissolved oxygen or ORP (only need to monitor one of the drains)
- Reclaim/Miscellaneous Drain Tank - cation conductivity mounted locally
Chemistry Program
The Basis for Cycle Chemistry Control

- To form the proper protective passive layer.
- To protect this passive protective layer during operation.
- To protect this passive protective layer during shutdown.
Protective Passive Layer
All boiler tube and turbine blade failures influenced by cycle water chemistry have the breakdown of the passive protective layer as part of the failure mechanism.

If you protect your protective layer 24/7 seven days a week 365 days a year, you will not have boiler or turbine blade failures due to cycle chemistry.
Water Chemistry Influence on Boiler Tube Failures of Supercritical Units

- Corrosion Fatigue
- Pitting
- Stress Corrosion Cracking
- Supercritical Water wall Cracking
Cracking mechanism in which cracks initiate and propagate due to combination of cycle tensile stress and environmental which is corrosive metal

**Process of developing cracks**

- Bretel iron oxide layers fractures, opening microscopic cracks through metal surface
- Exposed metal at the root of crack oxide forms a notch
- During cycle of tensile stress, the oxide fractures at the notch, and cracks are depend
- The cycle continuous a wedge shaped cracks propagate through the metal
Corrosion Fatigue

Cause:

- Rapid cycle cooling
- Rapid startup and shutdown
- Operation at low pH and excessive high O2 promote pitting. This pit serve as stress concentration to initiate corrosive fatigue cracks
This is Corrosion Fatigue
Control of dissolved oxygen - Ensure unit has been paralleled for a minimum of 2 hours prior to closing DA vent.

Control of economizer inlet pH - trip unit when EI pH drops below 7.0

Stress, heat up and cool down rate do not exceed OEM recommendations
Pitting and Stress Corrosion Cracking
- Sulfate and/or Oxygen + water
- Happens when unit is shutdown
  - Operation at low pH level or excessive high O2 promotes pitting
Ensure deaerator vent is open and cycle pH is increased on removal of unit from service

- Trip unit if EI cation conductivity is 2.0 m mho for 5 minutes or 5.0 mmho for two minutes.

- Trip unit if EI pH drops below 7.0.
Metal failure resulting from a combination static tensile stress and a specific corrodant to which metal is sensitive

Chlorides + Water

Initiated on shutdown

Propagates during operation
▪ Ensure deaerator vent is open and cycle pH is increased on removal of unit from service

▪ Trip unit if EI cation conductivity is 2.0 mmho for 5 minutes or 5.0 mmho for two minutes.

▪ Trip unit if EI pH drops below 7.0.
Damage generally forms as regular, parallel cracking, typically oriented circumferentially.

The primary root cause is the buildup of excessive internal deposits in the tubes.

Thermal or stress cycles with heavy internal deposits leads to supercritical waterwall cracking.
Supercritical WaterWall Cracking
Trip unit if EI cation conductivity is 2.0 mmho for 5 minutes or 5.0 mmho for two minutes.

Trip unit if EI pH drops below 7.0.
Turbine Deposition
LP Turbine Rotating Blade
Deposition caused by Steam Chemistry

- Causes include sodium (EI sodium analyzer), chlorides (EI cation conductivity analyzer), and sulfates (EI cation conductivity analyzer) within a moist environment.

- These contaminants can lead to pitting which can turn into stress corrosion cracking or corrosion fatigue turbine blade failures.
- Silica contamination will deposit on the back end of the LP turbine. Silica will cause some efficiency loss of the LP turbine.

- Silica needs to be maintained below 10 ppb in steam. (Silica Analyzers)
Trip unit if Eco inlet cation conductivity is 2.0 mmho for 5 minutes or 5.0 mmho for two minutes.

Trip unit if El pH drops below 7.0.

Trip unit if El sodium increases above 24 ppb (action level 1 starts at sodium > 3 ppb).

Analyzer alarms