VI. HEAT RECOVERY STEAM GENERATORS (HRSG) and TREATMENT CHEMISTRIES
Heat Recovery Steam Generators (HRSG)

- HRSG – ‘Steam-Raising Waste Heat Boilers’. A typical oil refinery may have 30 or more HRSG’s.
- HRSGs – commonly employed in smaller electrical power generators using diesel engines or gas turbine engines.
- Combined-Cycle and Cogeneration applications where heat from the exhaust of a combustion turbine is used to produce steam for additional power production or other industrial purposes.
- Combined-Cycle units operate up to 60% efficiency, burn natural gas or oil, and easily installed in a short period.
Heat Recovery Steam Generators (HRSG)

- HRSG’s – a key component in a Combined-Cycle or Cogeneration units.
- Several HRSG variations: Vertical Tube Drum-type, in which a single drum boiler is placed within the gas path.
- Natural or forced circulation, and once-through boilers are also available.
- The unique features of HRSG designs and particularly those of multiple pressures, make boiler water treatment, chemistry and control a critical and challenging task!
- High cycling HRSG’s are particularly vulnerable to problems such as FAC.
Erosion, Flow Accelerated Corrosion (FAC), Erosion - Corrosion and Cavitation Erosion

• *Erosion* – damage resulting from water, steam, and/or particulates on a material.

• *Erosion* – evident as etching, distinct lines, or the wallowing out of a certain area; chemistry and velocity can be causative; often misdiagnosed as *Flow Accelerated Corrosion (FAC)*.

• *FAC* – *Flow Accelerated (or Assisted) Corrosion* is defined as a process in which the normally protective oxide layer on carbon or low-alloy steels dissolves into a stream of flowing water or steam-water mixture.

- FAC can occur in single- and in two-phase regions, predominantly in the LP Section of the HRSG.
- Chrome steels are required in this section of the HRSG.
Differences Between Erosion, FAC, Erosion-Corrosion, and Cavitation Erosion

- *EPRI* has stated that the cause of FAC is water chemistry. Two phase FAC can be differentiated between *Cavitation* by the evidence of ‘tiger stripes’ or ‘chevrons’.
- FAC, often generically classified within the industry as *Erosion-Corrosion*, is a term originating with *EPRI*.
- *EPRI* defines *Erosion-Corrosion (EC)* as ‘the degradation of material caused by both mechanical and chemical processes.’
- FAC is often mislabeled as *Erosion-Corrosion*, even though FAC is caused by chemical and mass transfer effects.
Differences Between Erosion, FAC, Erosion-Corrosion, and Cavitation Erosion

• The term *Erosion-Corrosion* includes many erosion and corrosion mechanisms, while the term *FAC* is very specific.
• It would not be incorrect to call *FAC* erosion-corrosion. However, *FAC* refers to a specific set of erosion-corrosion conditions.
• While general industry practices in identifies *FAC* as *Erosion-Corrosion*, there are no mechanical processes associated with *FAC*. 
Differences Between Erosion, FAC, Erosion-Corrosion, and Cavitation Erosion, contd.

- **Cavitation Erosion (CE)** – occurs downstream of a directional change or in the presence of an eddy, and is identified by round pits; often misdiagnosed as FAC.

- **CE** also involves fluids accelerating over the surface of a material but unlike erosion, the actual fluid is not doing the damage.

- Cavitation results when small bubbles in a liquid strike a surface. These bubbles form when the pressure of a fluid drops below the vapor pressure (the pressure at which a liquid becomes a gas); when these bubbles strike the surface, they collapse or implode.
Differences Between Erosion, FAC, Erosion-Corrosion, and Cavitation Erosion, contd.

- A single bubble imploding does not carry much force but, over time, the small damage caused by each bubble exhibits cumulative effects.
- The repeated impact of these implosions results in the formation of pits.
- Similar to erosion, the presence of chemical corrosion enhances the damage and rate of material removal.
- Cavitation is not a property of a material, but of the system itself. A fluid’s pressure is determined by the size and shape of the vessel, not the material. While a stronger material can be highly resistant to cavitation, no metal is immune.
Water Tube HRSG from Gas Turbines

Waste Heat Recovery Boilers used with Gas Turbines provide 1 - 15 MW, up to 40 MW with a steam pressure up to 60 bar and Superheated Steam up to 450°C.

- HRSG is a strategic part of a Combined Heat & Power (CHP) industrial system recovering the waste heat of exhaust gases from Gas Turbines.
- Benefits: High Thermal Efficiencies; Reduced Thermal Emissions; Improved Overall Energy Economics.
Typical Design Features of GT HRSG

• **Drums**: The upper and lower drums are installed crosswise to the GT flue gas flow. The internal steam drum provides for high steam purity due to a wide steam scrubber and free end-flow, to minimize turbulence and level fluctuation.

• **Primary Steam Generation**: Uses a convection Steam Heater (SH) consisting of sections of fully drainable, vertical-finned tubes or smooth-type coils with multi-pass steam flow and gas cross-flow.

The SH, installed in the first part of the convection section of the boiler, is shielded by a number of screen tubes in order to avoid creep fatigue failure due to exposure at high temperatures over a long period.
Typical Design Features of GT HRSG, contd.

• **Convection Section:** The HRSG tube bank consists of a series of tubes properly bent and welded to the external headers. The outer tubes forming the external wall are membrane, providing a continuous gas enclosed *Membrane Wall*.

• **Economizer:** The HRSG *Economizer* recovers waste energy from the flue gases downstream of the convection section and transfers it to the boiler feedwater, increasing thermal efficiency and reducing thermal emissions.
Two-Stage Combined Cycle Gas Turbine and HRSG Steam Turbine Electricity Generation
Two-Stage Combined Cycle –
First Stage Gas Turbines
HRSG Operation Problems

• Most large new combined cycle plants in the US were designed under the assumption that they would be base-loaded, or at least infrequently cycled. This basic assumption has proven to be far from the actual operating modes for most new plants as gas energy prices have fluctuated widely in recent years.

• Two-Shift cycling is now common and is differentiated from Seasonal Duty, where plants are run essentially base-load but only for a few months of the year.
HRSG Operation Problems, contd.

• Since combustion turbine ramp rates and startup procedures directly affect HRSG component temperature ramp rates, the push to rapid Combustion Turbine (CT) startups results in greater ramp rates in HRSG hot section components than was assumed in plant design analyses.

Larger thermal stresses result with significant implications for the fatigue life of affected components such as drums, thick section headers, and tube-to-header welds.
Additional HRSG Operational Problems

- Cycling produces a rapid thermal response, which results in more condensate accumulation during startups and a greater requirement for attemperation spray to control piping metal temperatures.

- The extreme conditions that are caused by cycling operations sometimes result in water-hammer in affected piping systems, thermal quenching of hot component surfaces, and in some instances, leakage or failure of the pressure boundary at tube-to-header welds, riser piping to drums, crossover (connecting) piping, and drain connections.

- Cold weather operations also provide a different challenge with the need to maintain temperature to prevent header failure from freezing conditions.
Additional HRSG Operational Problems, contd.

Many new combined-cycle plants have experienced premature failures leading most operators to pursue a more aggressive approach to assure that HRSG component integrity is verified by periodic inspections more detailed than ‘statutory boiler inspections). For example:


2. Ultrasonic Testing (UT) of wall thickness for selected (high risk) tubes and header and riser components in order to establish the condition of HRSG components early in their service. Drum baffle plates and cyclone separator ‘can’ thicknesses are also measured.
3. Visual inspection of accessible HRSG water-side components including: primary and secondary steam separation devices; feedwater penetrations; instrument and blowdown penetrations; and baffle plates and their mechanical restraints (bolting and/or welds).

Plants with a history of HRSG component damage may also schedule:

- Dye Penetrant (PT) inspection of areas susceptible to cracking.
- Radiographic Testing (RT) of tube-to-header welds (suspicions of weld defects or sub-surface cracks).
- Thermography of HRSG casings to identify hot spots and more thorough examination of older units with more accumulated operating hours.
Additional HRSG Operational Problems, contd.

- Boroscope inspections are relatively uncommon for large HRSG components due to a general lack of access to areas of interest.
- Boroscopes are used to inspect attemperator spray liners.
- Attemperator sprays have been a significant problem especially due to a tendency to ‘overspray’ in order to control metal temperatures in Reheater and HP Superheater outlet piping to below design values for units subject to heavy cycling.
Dewpoint and Chloride Stress Corrosion Cracking - Combined Cycle Cogeneration Facility
Failed HRSG Gas Baffle
Failed Casing Seal Weld Around Reheat Connector to Lower Manifold
Buckled Liner Plates in Firing Duct
Cycling Unit: Kinks in Reheater Tube
Bowed Reheat Tubes Due to Water-Hammer
Cycling HRSG: Fatigue Failure of 304H Stainless Steel Reheater Tube Stub
Cycling HRSG: Stress Corrosion Cracking Failure in LP Feedwater Tube
Cycling HRSG: Leaking 16” Reheater Crossover Link Tube
Water Chemistry: Sticky Deposits (pH 3.0) on LP Economizer Tubes
Water Chemistry: Ammonium Bisulfite Accumulation on Final Row of Feedwater Heater Tubes
HRSG: Flame Impingement on Downstream Tubes
HRSG Water Chemistry Control

• In some multi-pressure HRSG’s, the low-pressure (LP) boiler serves as a feedwater heating source for intermediate- (IP) and high-pressure (HP) boilers.

• An All-Volatile Treatment (AVT) would probably be the best choice for the LP boiler, so that the water remained low in dissolved solids.

• Congruent or Coordinated Phosphate would be a reasonable choice for the IP boiler and possibly the HP boiler, depending upon the severity of hideout.

• Combined-cycle units are often cycled frequently. Cycling puts more stress on boilers and boiler water chemistry than any other aspect of operation. Cycling also has more influence on the frequency of chemical cleaning than any other factor.
• Each steam generating network in a multiple-boiler HRSG operates at a different pressure. Intermediate pressures may range from 200 to 500 psig, with low-pressure boilers operating from as low as saturation pressure to around 100 psig. The different pressures require different chemistry control regimes.

• The low-pressure boiler may directly supply feedwater to the intermediate-pressure and high pressure steam generators. This factor dictates additional chemical treatment requirements for the low-pressure boiler.

• The deaerator may be integral to the low pressure boiler.

• Flow rates in HRSG’ s are generally higher than in conventional boilers. This increases the possibility of flow-assisted corrosion.
HRSG Water Chemistry Control, contd.

- Blowdown may be cascaded from high-pressure boilers to low-pressure boilers as an energy saving technique.

- Makeup water requirements can be quite large for cogeneration units, where part or all of the steam may be consumed in an industrial process.

- Heat fluxes in HRSG boilers are lower than those in standard fossil-fueled units, in part because the boilers are not exposed to radiant heat.

- Lower heat fluxes reduce scaling and corrosion potential. However, this advantage may be offset by increased cycling.
HRSG Water Chemistry Control, contd.

Hydrazine

• Several difficulties have arisen from using Hydrazine. The most troubling problem is Flow Assisted Corrosion (FAC). In completely deoxygenated environments, flowing water will erode carbon steel, particularly at pipe bends and other flow disturbances. Several catastrophic FAC-induced failures, some causing fatalities, have occurred within the past decade.

• FAC is greatly minimized if a slight oxygen residual is allowed to remain in the feedwater, such that the protective magnetite layer is maintained on the pipe walls. A dissolved oxygen residual of 1 to 2 ppb is recommended. For this reason Oxygenated Treatments (OT) have developed.

• FAC in HRSG’s may be even more severe, due to the higher flow rates. This can be combated by fabricating elbows out of higher grade materials, such as the 1.25 Cr-0.5 Mo or 2.25 Cr-1.0 Mo steels.
Alternate Oxygen Scavengers

• They are more expensive and will break down in boilers to form organic acids and carbon dioxide, which in turn will carry over to turbines and other after-boiler equipment.

• Debate goes on regarding the corrosive effects on turbine blades of the carryover products.
Oxygenated Treatment (OT)

- OT, in which oxygen is deliberately injected into the feedwater system, was developed in Germany about 25 years ago for replacement of all-volatile treatment (hydrazine/ammonia) in once-through steam generating units.

- The treatment involves the controlled injection of oxygen or hydrogen peroxide into the condensate/feedwater system. The controlled feed causes the magnetite layer on the pipe walls to become overlayed and interspersed with an even tighter film of ferric oxide hydrate (FeOOH). This compact layer is more stable than magnetite and releases very little dissolved iron or suspended iron oxide particles to the fluid.
Oxygenated treatment (OT)

• Some once-through utilities that switched from AVT to OT have reported that dissolved feedwater Fe concentrations, which were often 10 ppb or higher on oxygen scavenger programs, dropped to as low as 1 to 2 ppb once the OT program was fully established.

• In the most popular OT program, known as Combined Water Treatment (CWT), oxygen is dosed to maintain a 50 to 150 ppb residual. Ammonia is added to raise the pH to 8.0-8.5. Typically, 20 to 70 ppb of ammonia will produce this pH.

• OT is a very real consideration for once-through HRSGs. One drawback is that OT requires extremely pure makeup and feedwater, which mandates the use of a condensate polisher.
pH Control

• Excursions of pH outside a relatively narrow range will induce corrosion.

• Feedwater piping and heat exchanger tubes exhibit minimal corrosion at a mildly alkaline pH. For a feedwater system containing all steel metallurgy, the optimum pH range is 9.0 to 9.6.

• Corrosion control in mixed-metallurgy systems is more complicated. Admiralty brass performs best within a pH range of 8.5 to 9. Copper-nickel alloys (particularly the 90-10 material) are most stable around a pH of 9.3.

• For a system containing carbon-steel piping and copper-alloy heat exchanger tubes, a recommended pH range with Admiralty materials is 8.8 to 9.1.
pH Control, contd.

- Ammonia and organic neutralizing amines are the pH conditioning chemicals of choice.

- Amines will decompose to produce ammonia in feedwater. Whether the ammonia comes from direct ammonia feed or amine decomposition, a general rule of thumb recommends that ammonia concentrations be limited to 0.5 ppm in systems containing copper-alloy materials. This level may be too high where excess air in-leakage may occur.

- In systems with turbines, decomposition of amines can potentially introduce unwanted organic acids and CO₂ into the turbine. Some experts recommend ammonia over all other pH conditioning chemicals, others are not convinced!
Phosphate Treatment

• Phosphate *hideout* and incongruent precipitation of Na$_3$PO$_4$ on tube walls can be problems.

• TSP is most soluble at 250° F, but solubility rapidly falls off and becomes very low at 600° F. The effect may become very pronounced in units above 2,000 psi and/or are subjected to frequent load changes. Hideout depletes the boiler water of the chemical designed to control chemistry. The phosphate compounds often precipitate incongruently, with deposit sodium-to-phosphate molar ratios of 2:1 or lower, causing "acid phosphate corrosion".
Phosphate Treatment, contd.

• *Hideout* can be at its worst in a cycling unit. Shutdowns and startups, and even load changes, cause precipitation and dissolution of phosphates. This in turn causes wide fluctuations in boiler water chemistry. Severe hideout and the reverse dissolution process have been known to force boiler water pH below 7 in cycling units.

• Phosphate *hideout* appears to be further influenced by the cleanliness of the boiler tubes, and becomes more severe with increased deposit loading, particularly iron oxides. The evidence indicates that sodium phosphates form a sodium-iron-phosphate complex with the magnetite layer. Periodic boiler chemical cleanings can potentially reduce *hideout* by minimizing the presence of porous magnetite deposits.
HRSG Water Chemistry Control, contd.

Phosphate Treatment, contd.

• Lower heat fluxes in HRSG’s tend to reduce PO$_4^{3-}$ deposition. Frequent cycling is a problem.

• Equilibrium Phosphate Treatment (EPT) is designed to minimize *hideout*. Phosphate residuals are maintained within a range of 0.2 to 2.5 ppm, and pH within a range of 9.0 to 9.7.

Alkalinity is controlled by the addition of trisodium phosphate with supplemental addition of caustic, generally at unit startup. This treatment produces a solution with a sodium-to-phosphate ratio of 2.8:1 or greater, with most of the control range at 3:1 or above. Caustic alkalinity is from 0 to 1 ppm.
Caustic Treatment

- In a caustic treatment program, boiler water pH is maintained within a range of 9.4 to 9.6 by addition of caustic to maintain an NaOH level of 1.0 to 1.5 ppm.

- Feedwater chemistry must be well controlled to prevent excessive deposit formation in the boiler, which might lead to under-deposit caustic corrosion. Sodium nitrate is frequently added with caustic to prevent stress corrosion cracking of boiler tubes.

- As is the case with EPT, the higher levels of caustic in the boiler water may lead to greater carryover of sodium hydroxide to the turbine.
All-Volatile Treatment

- AVT was developed mainly for once-through boilers and is a combined feedwater/boiler-water treatment program. Ammonia or amines and an oxygen scavenger carry through the boiler into the steam.

AVT guidelines for a once-through unit call for a pH range of 9.3 - 9.6 with less than 2 ppm dissolved solids. Ammonia levels from 1-2 ppm. Condensate polishers are an absolute requirement.

- AVT is also used in some drum boilers, especially near critical pressure (3,203.6 psia). AVT does not protect drum boilers from contaminant introduction due to a condenser leak or other problem.

Condensate polishers are the most effective buffer against chemistry upsets.
All-Volatile Treatment, contd.

- AVT has lost a lot of popularity as it tends to increase carryover of chloride and sulfate, which then deposit on the LP turbine blades. In addition, amines and organic oxygen scavengers can break down into CO$_2$ and organic acids, which are potentially corrosive to turbine blades and after-boiler components.

- OT has proven to be much better at minimizing feedwater system and boiler corrosion.
AVT and Ammonical Corrosion

In systems where ammonia is used, *ammonical corrosion of steel* can occur when oxygen is present and the pH is over 8.3.

Copper, its alloys, and other non-ferrous metals are attacked and severe damage results due to the formation of a stable cupric ammonium complex ion.

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\text{Cu} + 4 \text{NH}_3 + \frac{1}{2} \text{O}_2 \rightarrow \text{Cu(NH}_3)_4^{2+} + 2 \text{OH}^-
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