Implementation of water chemistry in fossil power plants with drum boilers and in combined cycle/HRSG plants

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Abstract. Current water chemistry practice at fossil power plants with drum-type boilers and heat recovery steam generators includes ammonia dosing into the feedwater train and sodium phosphate or sodium hydroxide into the boiler water. The issues and impact on equipment with the use of phosphate or sodium hydroxide boiler water treatment, as well as optimum conditions for the use of these chemicals are discussed. Another operational issue of boiler unit is associated with flow-accelerated corrosion (FAC) of material, especially in the low-pressure circuit. The major reasons for boiler failures are outlined, with the data on FAC failure locations. An effect of oxygen and ammonia on boiler corrosion processes is discussed.

At present, the following water chemistries are used at fossil power plants with high and ultrahigh drum-type boilers:

- All-volatile treatment (ammonia and hydrazine or ammonia feed) of feedwater train and sodium phosphate treatment of boiler water;
- All-volatile treatment (ammonia and hydrazine or ammonia feed) of feedwater train and sodium hydroxide treatment of boiler water;
- Oxygenated treatment (oxygen and ammonia feed) of feedwater train and sodium hydroxide treatment of boiler water;
- Filming amine treatment of feedwater train.

The major aim of these treatments is to reduce corrosion rate of materials and minimize deposition in water and steam train of power-generating unit.

Of the above treatments, the most common one is the feed of phosphate in the boiler water. There are three types of phosphate treatment used worldwide [1]:

- Congruent Phosphate Treatment (CPT), with feed of tri- and di- and/or mono sodium phosphate; ratio between Na and PO₄ is lower than 2.6;
- Equilibrium Phosphate Treatment (EPT), with feed of trisodium phosphate and NaOH; concentration of NaOH does not exceed 1 ppm, ratio between Na and PO₄ is higher than 3;
- Phosphate Treatment (PT), with feed of trisodium phosphate only; ratio between Na and PO₄ is 3.

More than 80% of the fossil plant drum-type boilers operate with CPT at ratio between Na and PO₄ lower than 2.6. Under these conditions, acid phosphate corrosion could occur, especially in the presence of large amount of deposits on heat exchange surfaces, and phosphate hideout takes place. Use of EPT does not cause acid phosphate corrosion, and concentration of phosphate in many boilers was reduced to 0.2 ppm. However, under these phosphate levels, the metal protection against impact of acid corrosion substances is reduced, resulting in hydrogen embrittlement of metal. Similar processes also occur in...
HRSGs, with flow-accelerated corrosion (FAC) and hideout prevailing in low-pressure and high-pressure circuits respectively.

Based on more than 20-year fossil power plant operational experience worldwide, International Association for the Properties of Water and Steam developed water and steam purity limits for phosphate treatment at conventional power plants and heat recovery steam generators (HRSG) cycles [1]. In accordance with this technical guidance, it is recommended to use trisodium phosphate only or in combination with NaOH feed in concentrations below 1 ppm. Na:PO\textsubscript{4} ratio should be kept at 3:1 with feed of Na\textsubscript{2}PO\textsubscript{4} only, or should be higher than 3:1 with feed of Na\textsubscript{3}PO\textsubscript{4} and NaOH. Value of pH should not be lower than 9.0, with minimum concentration of phosphate being 0.3 ppm and higher.

Phosphate treatment of boiler water can be used over wide range of temperatures and pressures up to pressure 19 MPa. However, it should be emphasized that occurrences of hideout and hideout return increase with pressure and could take place already at 10 MPa. This is associated with negative solubility coefficient of phosphoric acid sodium salts: sodium phosphate solubility in boiler water decreases with temperature increase. Phosphate hideout during pressure increase results in associated change of boiler water pH. This pH change depends on type of phosphate treatment (i.e., on used chemicals). PT (feed of trisodium phosphate only) results in boiler water pH decrease during startup with increasing pressure and pH increase during shutdown. When di- and/or mono sodium phosphate is used (Na:PO\textsubscript{4} ratio is less than 3:1), pH increased during startup and decreases during shutdown. Tube deposits, especially at high pressures, promote interaction of acidic sodium phosphate salts with magnetite on metal surface, resulting in magnetite dissolution and occurrence of acid-phosphate corrosion [2]. Use of trisodium phosphate only does not generate reactions which result in metal corrosion, in contrast with CPT, when Na:PO\textsubscript{4} ratio is less than 3:1. In some cases hideout is so significant that power plant operators reduce phosphate levels down to 0.2 ppm (i.e., below minimum 0.3 ppm per technical guidance [1]). In this case it is recommended to feed not only Na\textsubscript{3}PO\textsubscript{4}, but also NaOH, into water, provided that relationships between phosphate levels, pH, and Na:PO\textsubscript{4} ratio are kept.

Alkaline treatment of boiler water (typically with NaOH) is done in drum-type boilers for reduction of pitting corrosion and hydrogen embrittlement, which are enhanced by the presence of chloride in water. Use of NaOH requires thorough monitoring of carry-over of impurities into steam, because increased levels of impurities in steam could result in stress corrosion cracking-induced failures in steam pipeline and turbine. These failures primarily are associated with the following materials: austenitic steels, stellites, steels with elevated stresses in superheaters and turbines. These issues, however, could be resolved by control of upper limit of boiler water pH with NaOH levels not exceeding 1.5 ppm [3]. Ideally, in order to prevent under-deposit corrosion, alkali concentration should be selected with account for chloride level in boiler water. It should be emphasized that alkaline treatment can only be performed in boilers with good circulation with virtual absence of “dry zones” on the equipment surface. Alkali feed can make on-line water and steam monitoring easy.

Upper limit of sodium and other ions in boiler water is governed by their limits in steam, which these impurities can entrain due to mechanical and vapoaurous carry-over. Mechanical carry-over is the major cause for contamination of steam with NaOH, because at pressures below 17 MPa its distribution ratio between boiling water and steam is insignificant. This factor should be taken into account, especially during frequent equipment startups and shutdowns. Concentration of NaOH in boiler water should be adequate to neutralize adverse effect of corrosive impurities, in particular, chloride. One of potential solutions is to bring NaOH levels in boiler water up to certain values: it should be 2.5 times higher compared to chloride level [3].

Major corrosion-related issues in HRSGs occur in the low-pressure circuits which operate at pressures 0.6–0.8 MPa and temperatures 150–178 °C. The major failure causes in HRSGs are given in Table 1 [4, 5].

Thus, in boilers the following corrosion types can be found: pitting corrosion, stress corrosion, corrosion fatigue, FAC, under-deposit corrosion; also, deposition takes place. However, the basic equipment failure cause in low-pressure boiler circuits is FAC (Table 2), and in high-pressure circuits – deposition [6].
Table 1. Causes of failures in HRSGs at combined power plants.

| Failure Location                                      | Failure Cause                  |
|-------------------------------------------------------|--------------------------------|
| Feedwater heater                                      | Pitting corrosion              |
|                                                       | Stress corrosion cracking      |
| Low-pressure HRSG evaporating circuit                 | FAC                            |
| Economizer                                            | Pitting corrosion              |
|                                                       | Stress corrosion cracking      |
|                                                       | Corrosion fatigue              |
|                                                       | Deposition                     |
| High-pressure HRSG evaporating circuit                | Pitting corrosion              |
|                                                       | FAC                            |
|                                                       | Under-deposit corrosion        |
|                                                       | Gas-side corrosion             |
| Superheater                                           | Gas-side pitting corrosion     |
|                                                       | Gas-side general corrosion     |
|                                                       | Wall overheating               |
|                                                       | Metal creep                    |

Table 2. Major Locations of Failures in HRSGs at Combined Power Plants [7].

| Equipment Type                                      | Failure Location                      | Failure Type                               | Failure Cause                                                                 |
|-----------------------------------------------------|---------------------------------------|--------------------------------------------|-------------------------------------------------------------------------------|
| Vertical boilers with forced circulation,           | Low-pressure evaporating circuit (tube| Wall thinning; Development of surface      | Elevated velocities (up to 20 m/s) of water-steam mixture in the upper low-     |
| horizontal tubes                                    | bends, piping)                        | roughness; Crack formation                 | pressure evaporating circuit with small tube diameter; Lack of bottom draining  |
|                                                     |                                       |                                            | for periodic blowdown and sludge removal                                         |
| Horizontal boilers with natural circulation,        | Low-pressure evaporating circuit (tube| Wall thinning; Development of surface      | Low circulation velocity in some tubes; Elevated thermal and mechanical stresses in tubes under cyclic loads |
| vertical coils with drains                          | bends, piping)                        | roughness; Crack formation                 |                                                                 |

Under these temperature conditions, FAC is largely enhanced in tube bends by water hammer effects and increased flow turbulence, resulting in change in mass transfer and dissolution of magnetite protective film. Presence of liquid phase in two-phase fluid enhances mechanical impact of moving flow on material with increased breakdown of protective oxide film on metal surface. Water droplets can form liquid film on metal surface, especially in and around tube bends, where corrosive impurities concentrate in accordance with distribution ratio between steam and liquid phases; these corrosive impurities enhance corrosion processes. Figure 1 shows boiler locations which are most susceptible to FAC [8].

Since FAC rate depends on material composition and flow velocity, it is recommended to use high-chromium steels in the areas with high susceptibility for FAC.

It was mentioned above that water chemistry is one of the FAC-influencing factors. Operational experience of overseas fossil power plants shows that FAC rate in oxygenated environment is significantly low, in so doing, oxygen concentration should be adequate for passivation of entire boiler feedwater train. FAC rate is typically estimated by iron concentration, which should be 2 ppb and lower in turbine condensate, and in all boiler water circuits should not exceed 5 ppb [1].
Figure 1. Major FAC-prone locations in horizontal boiler [8].

Oxygen alone, acting as oxidizing chemical, is not capable to reduce FAC rate, because it goes to steam due to high distribution ratio between water and steam: this distribution ratio at operational conditions of the low-pressure circuit is about 4·10^4. Absence of oxygen in liquid film on material surface significantly reduces rate of protective film formation. Therefore, feed into coolant of chemicals that increase liquid phase pH is needed. In accordance with international guidelines, feedwater pH should be kept within 9.2–9.8 with ammonia feed, and boiler water pH (low-, medium-, and high-pressure circuits) – within 9.0–9.8 with NaOH or Na_3PO_4 feed.

Use of AVT with ammonia feed also poses boiler pH-related issues caused by large distribution ratio between boiling water and saturated steam. Therefore, in order to keep desired boiler water pH, it is necessary to feed either ammonia in very high concentrations, or NaOH or Na_3PO_4.

Feed of integrated (complex) polyamine chemicals creates more favorable conditions for maintaining uniform pH values in the water-steam cycle; in addition, filming amine-based corrosion-protective film is formed on material surface [9].

References
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