Cycle and Harm of Main Pollutants in Thermal System of Gas Turbiner

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Abstract. This project analyzes and studies the monitoring data of chemical water vapor in the operation of a gas steam combined cycle generator unit, discusses the accuracy, measurement error and the correlation among various water vapor indexes of the (hydrogen) conductivity, pH value, sodium content, dissolved oxygen, silicate root, phosphate root and other monitoring experiments in the water vapor quality monitoring work, and puts forward the condensate and water supply which are easy to be measured accurately. Based on the hydrogen conductivity of saturated steam, superheated steam and the conductivity of boiler water, estimated the chlorine content, ammonia content, pH value and other indicators of water (steam) at each sampling point, comprehensively judged the accuracy of water quality measurement, prevented serious deterioration of water vapor quality, and ensured that the thermal equipment is free from corrosion, salt deposition and scaling.

1. Introduction

Large scale gas steam combined cycle power generation unit is a whole thermal cycle composed of gas turbine and steam turbine, which has the characteristics of high efficiency, energy saving and environmental protection. It has been applied and developed in the developed areas of economy in China, which puts forward new requirements for the traditional chemical supervision of power plants, and analyzes the steam products of this type of unit in operation quickly and accurately. Ensuring the accuracy of analysis data, it is of great significance to prevent thermal equipment from corrosion, salt deposition and scaling, and to ensure the safe, stable and economic operation of the unit.

At present, the main problems existing in the supervision of water and steam in power plants are that the control of water and steam indexes is not strict, the qualified rate of water and steam quality is low, the water quality is not controlled according to the indexes specified in the regulations, and remedial measures can be taken after the water quality is abnormal, and even the remedial measures taken by different power plants are not timely and reasonable. The above facts are relatively clear, and the problems are easy to judge. In some power plants, the water vapor quality detected during operation is good, and the qualified rate of water vapor quality is very high. However, during overhaul inspection, it is found that the corrosion or deposition rate of thermal equipment is high, and the corrosion, salt deposition and scaling are relatively serious. There are many reasons for this situation. First of all, it may be that the water vapor index is not reasonably formulated, and the equipment, operation condition, water source and surrounding areas of each plant are all in good condition. The environment is different. We should not blindly quote standards. We should determine the water vapor index of our plant according to the standards and the actual production situation. If necessary, we need...
to determine it through thermochemical experiments. The second possibility is that the supervision and measurement are not accurate, and the incorrect supervision data will inevitably lead to incorrect results. On the surface, the water vapor quality is qualified, in fact, many problems are covered. The water and steam index control is not strict, the water and steam quality qualification rate is low, and even the thermal equipment is corroded, salted and scaling. The main reason is the management problems. The power plant should improve the understanding of chemical supervision work, increase the strength of equipment management, strengthen the professional training of employees, do a good job in accident prediction of various abnormal conditions, and actively respond to them. If the water vapor index is unreasonable, it should be redetermined according to the standard. If necessary, scientific research units should be invited to assist. It is necessary to strengthen the management of laboratory and on-line chemical instruments to ensure the accuracy of supervision and detection, so that on-line analytical instruments such as conductivity, pH value and dissolved oxygen have higher input rate and accuracy rate.

2. Cycle and harm of main pollutants in thermal system
During the operation of the unit, in addition to the normal addition of ammonia and phosphate, there are also some pollutants that leak into the thermal system, the main components of which are CO2, O2, silicate, sodium salt, Ca2+, Mg2+, Cl-, PO43-, iron oxide, ammonia, grease, etc. These pollutants enter the thermal system and flow with the water vapor circulation, some of which are connected with other substances and thermal equipment in the water under the conditions of temperature, pressure, etc. The prepared metal reacts physiologically or decomposes and fission itself. The residual pollutants and reaction products continue to circulate with the water vapor, some are discharged with the sewage, some are removed by the deoxidizer and other devices, some are deposited on the metal surface of thermal equipment to form salt or scale.

2.1. Cycle and harm of phosphate in thermal system
Phosphate mainly enters the thermal system through boiler water dosing to improve the pH value of boiler water and remove Ca2+ and Mg2+ ions from boiler water. When the pH value of boiler water is low, NaOH should be added. The phosphate in the boiler water reacts with Ca2+ ion to produce basic calcium phosphate, which is a kind of soft water slag. It is easy to be discharged with the boiler blowdown, and will not adhere to the boiler to form secondary scale. The phosphate content in the boiler water should not be too much, otherwise, it will not only increase the drug consumption, but also increase the salt content of the boiler water, affect the steam quality, and also easily produce phosphate concealment, even Mg3(PO4)2 scale. The amount of phosphate carried with steam dissolution is very small, so it can not be detected in steam by conventional methods during normal operation. Once phosphate is detected in steam water sample, it must be caused by water carried by steam. The phosphate that enters the turbine with the steam will precipitate on the throttle parts such as the valve, turbine blade, diaphragm, etc., forming phosphate scale. Slight phosphate scale will only leave white mark on the flow passage part. In serious cases, it will jam the opening and closing of important valves such as high-pressure main throttle valve and high-pressure regulating valve, even deposit on the turbine blade and diaphragm.

2.2. Cycle and harm of ammonia in thermal system
Ammonia enters the thermal system mainly through condensate and feed water dosing. Hydrazine and other deoxidizers decompose to produce ammonia. Adding ammonia to the thermal system can improve the pH value of condensate, feed water and boiler water to prevent acid corrosion. Ammonia circulates in the whole thermal system with water vapor. The ammonia content at each sampling point is relatively large. NH4+ is the cation with the largest amount in the thermal system, which makes the thermal system The pH value of the water vapor is maintained in the basic important ions. The first ammonia dosing point is at the outlet of condensate pump, where the ammonia content is about 350-550μg·L⁻¹. Ammonia circulates with condensate into low-pressure evaporator and low-pressure steam
drum, and part of ammonia is removed at the same time of thermal deaeration. Because the distribution coefficient of CO₂ and ammonia (the ratio of the concentration of a substance in steam to its concentration in water) is greater than 1, and the distribution of CO₂. The coefficient is much larger than the distribution coefficient of ammonia. The amount of CO₂ removed in the thermal deaerator is more than that of ammonia removed. The amount of ammonia left in the water is higher than that of CO₂. The pH value of deaerator outlet water is higher than that of inlet water. The second ammonia dosing point is at the inlet of the feed pump. At this time, the ammonia content recovers to 500-1000μg·L⁻¹ again. With the feed water entering the high-pressure evaporator, a large amount of ammonia volatilizes from the evaporator to the steam and flows with the steam. In the last stage of low pressure cylinder of steam turbine, there is a small amount of steam condensed after doing work, which contains about 10% of wet steam, especially when the vacuum control of condenser is not good, the steam humidity of the last stages of low pressure cylinder is high, and even condenses into small water drops, part of ammonia, Cl⁻, low molecular organic acids, etc. carried by steam dissolve into water, but because the distribution coefficient of ammonia in vapor-liquid phase is greater than 1. The reason for this is that the amount of acid ions such as Cl⁻ and low molecular organic acid carried by the steam dissolves into the water is larger than the amount of dissolved ammonia. Most of the ammonia that used to maintain the pH value of the steam remains in the steam phase, and the pH value of the water phase is very low, which is easy to cause acid corrosion in this part. When the pH value of the steam is about 9, the pH value of the water phase is 7-8, and the lowest is about 6. At this time, if there is air leakage into the water excessive steam turbine, oxygen content or organic matter will aggravate acid corrosion. After the steam turbine works, the exhaust steam is discharged to the condenser, and ammonia is still contained in the steam phase, some of which will be pumped out by vacuum pump, and most of which will be dissolved in the condensate. The reason is that the distribution coefficient of CO₂ is much larger than that of ammonia. The pH value of the steam side of the condenser is lower than the pH value of the condensate, and the loss rate of ammonia in the condenser and deoxidizer is 20-30%. The ion with the largest content in condensate is NH₄⁺, which is about 500μg L⁻¹ in normal operation. Its molar concentration is almost 100 times of the total molar concentration of cations such as Na⁺, Ca²⁺, Mg²⁺, etc. ammonia also enters the heat network heater and various auxiliary steam heaters along with steam. The steam exchanges heat in each heater and condenses into hydrophobic water. The ammonia in the hydrophobic water is more than CO₂, and the pH value of hydrophobic water is higher than that of inlet steam. Ammonia circulates in the thermal system along with water vapor, and the ammonia lost in deoxidizer, condenser, condensate polishing and other places is supplemented by adding ammonia in condensate and feed water, and the amount in the system keeps the overall balance.

2.3. Cycle and harm of CO₂ in thermal system

The main ways for CO₂ to enter the thermal system are the carrying of make-up water, the leaking of condenser and all kinds of hydrophobic water returning to the thermal system. The impure drugs such as ammonia water and phosphate also carry CO₃²⁻ to enter the system. CO₂ enters the thermal system and hydrolyzes into CO₃²⁻ form. In the alkaline environment, CO₃²⁻ reacts with Ca²⁺ and Mg²⁺ ions to form calcium carbonate and magnesium carbonate scale. CO₂ also reduces the pH value of water vapor and increases the possibility of acid corrosion. Therefore, the amount of alkaline drugs such as ammonia water to maintain the pH value of water vapor and the regeneration consumption of condensate polishing mixed bed are increased. CO₂ circulates in the thermal system with water vapor. During operation, most of CO₃²⁻ in the condensate is removed by condensate polishing, but CO₃²⁻ will be dissolved in the outlet of polishing along with ammonia addition, and CO₃²⁻ and free CO₂ will also be contained in the drain water returning to the deoxidizer. It reacts with ammonia in the water to form (NH₄)₂CO₃, which is heated in the low-pressure heater and deoxidizer, and then decomposed into ammonia and CO₂ gas and removed in the deoxidizer. The residual CO₃²⁻ enters the boiler with the feed water, except for a small amount of deposition to form CaCO₃ and MgCO₃ scale, the rest is decomposed into CO₂ in the boiler water, and CO₂ flows to the condenser and heaters with the steam.
The circulating water leaked into the condenser contains CO$_3^{2-}$, which makes the CO$_3^{2-}$ of the condensate increase, and the extraction of the condenser will also discharge some free CO$_2$ gas. In order to reduce CO$_3^{2-}$ entering into the thermal system, it is necessary to strengthen the equipment management to ensure the tightness of the thermal system, to ensure the purity of the drugs added into the thermal system, to shorten the exposure time of the drugs in the air as far as possible, and to prevent the gas from dissolving in.

2.4. **Cycle and harm of Cl$^-$ in thermal system**

The main sources of Cl$^-$ ions are condenser leakage, heater and heat network drainage, demineralised water and impure drugs, which can be removed from the thermal system through boiler water blowdown. Cl$^-$ ion can cause corrosion to the stainless steel parts of thermal equipment, especially to the flow passage part of low pressure cylinder of steam turbine and other local areas. The high content of Cl$^-$ in the boiler water of high and low pressure evaporator will also damage the protective film of heater pipe and cause corrosion. The content of Cl$^-$ ion in circulating water is very high, reaching 50-200mg·L$^{-1}$, or even higher, which is 10000 times of the amount of Cl$^-$ ion in steam during normal operation. Leakage into condenser will cause serious pollution of condensate. The ammonia water added into the thermal system is required to be prepared with demineralized water, and the phosphate, NaOH, etc. are all above standards of analytical purity. Generally, the content of Cl$^-$ ions carried into the thermal system with drugs is very low. Under the operation mode of cogeneration, it is easy to carry a large amount of Cl$^-$ ions into the water supply source, mainly the heat network drainage, especially the softened water prepared by the ion exchange process as the heat network For the supply water source of circulating water, saturated salt water is used as the regeneration agent for resin regeneration liquid. There are a lot of Cl$^-$ residues, normally about 15-20mg·L$^{-1}$. The circulating water of heat supply network is continuously concentrated softened water, and Cl$^-$ reaches about 30-50mg·L$^{-1}$. The infiltration of trace circulating water of heat supply network from the heater of heat supply network will rapidly increase the Cl$^-$ ion content of water supply and boiler water, which will cause harm to thermal equipment. It can be seen that the key to reduce the harm of Cl$^-$ ion to thermal equipment is to ensure the tightness of thermal equipment such as condenser and heating network heater.

2.5. **Circulation and harm of dissolved oxygen in thermal system**

The dissolved oxygen in the thermal system is mainly carried by the make-up water and various kinds of drainage water returning to the thermal system, and entered by the leakage of the condenser and the intake air of the pump shaft seal. Keeping a certain concentration of dissolved oxygen in the thermal system is conducive to the formation of a dense oxide film on the metal surface, which plays a role in preventing corrosion, but at the same time, too high dissolved oxygen will increase the metal corrosion rate, especially easy to form oxygen corrosion on the water supply pipeline, economizer and other equipment. The way to control the dissolved oxygen is through thermal deoxidizer and chemical deoxidizer.

2.6. **Circulation and harm of sodium salt in thermal system**

Sodium salt enters into the thermal system mainly through boiler water dosing, feed water dosing and make-up water, return drainage and condenser leakage will also carry sodium salt into the thermal system. The sodium salt in condensate mainly exists in the form of ions, and its main sources are steam carrying, make-up water carrying and condenser leakage. During normal operation, the sodium content in condensate is about 5μg·L$^{-1}$. The recovered drain water will also contain sodium salt, especially in the drain water of the heating network heater with softened water as the water source. The main reason is that the content of sodium in the circulating water of the heating network is about 200000μg·L$^{-1}$ during operation, and the micro leakage of the heating network heater will inevitably increase the content of sodium in the drain water rapidly. During normal operation, the sodium content of feed water is about 3-5μg·L$^{-1}$. The main reason for the high sodium content of feed water during
the operation of the heating network heater is the leakage of the heating network heater. The sodium salt in the boiler water is the sum of the alkaline substance added and the feed water concentrated. The sodium ion is one of the several ions with the largest content in the boiler water. During the operation, it is necessary to control the sodium phosphorus ratio reasonably, adjust the pH value of the boiler water, and prevent the acid corrosion and alkaline corrosion of the boiler pipe. The situation and mechanism of the acid corrosion of the boiler treated with phosphate are relatively simple and easy to foresee, which is rare at present. However, the situation of alkaline corrosion is not easy to be detected. This is mainly due to the high content of sodium salt in the boiler water, which is easy to generate free NaOH in the local concentration of the boiler tube during the rapid load rise and fall of the boiler. Therefore, it must be paid great attention to. The scale formed in the boiler and the discharged water slag contain sodium salt. The sodium salt is also carried to the steam turbine, superheater and main steam system with the steam. Due to the change of steam pressure and other parameters, the sodium salt will deposit in the superheater and the flow passage part of the steam turbine. Therefore, it is necessary to reasonably control the quality of the boiler water and the operation mode of the unit to ensure the steam water separation effect of the boiler, reduce the mechanical carrying and prevent the steam carrying water, reduce the salt content of boiler water.

3. Conclusion
Through the above analysis, the main pollutants circulating in the thermal system will have different forms of corrosion, which is very harmful to the thermal system, so we must try our best to reduce the pollutants into the thermal system, and the removal of pollutants is also a very important work.

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