



Research Paper

Decomposition characteristics of humic acid in boiler make-up water in power plants



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HIGHLIGHTS

- Decomposition products of humic acid exert an influence on the pH values.
- Inorganic ions in decomposition products of humic acid are Cl^- , SO_4^{2-} , NO_3^- and F^- .
- TOC of the make-up water should be strictly controlled.

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ABSTRACT

The organic matter (OM) entering the water–steam cycle of a power plant has been considered as one potentially serious contaminant in the industry. Therefore, the thermal decomposition characteristics of humic acid (HA) were investigated at an elevated temperature in a stainless steel autoclave through ion chromatography and total organic carbon analysis methods. The concentrations of the impurity anions varied with the changes in HA concentration and pyrolysis time. In addition, the different contents of thermal decomposition products in the vapour–liquid environment were evaluated. Results show that the major inorganic decomposition products of humic acid at 350 °C are chloride, sulfate, nitrate and fluoride ions. The experimental results are expected to contribute significantly to the quality control of feed and make-up water in power plants.

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1. Introduction

With the increasing number of supercritical and ultra-supercritical units, the quality of boiler feed water has to meet strict requirements to avoid problems such as deposit formation, corrosion, and foaming. The contents of iron, sodium, copper and other impurity ions have been strictly controlled and their contraction should be within several $\mu\text{g/L}$ or less in the feedwater. In particular, the expected concentration of iron, sodium, copper is not more than 3, 1, and 1 $\mu\text{g/L}$ respectively. Meanwhile, the electrical conductivity of feed water is limited to less than 0.1 $\mu\text{S/cm}$ under different feedwater treatment conditions in the once-through boiler [1]. Nevertheless, dissolved OM, such as humic acid (HA), still exists in the make-up water. Thus, controlling total organic carbon (TOC) in the water–steam system is an important work for chemical supervision in fossil power plant [2–4]. The OM in a water–steam system is one possible cause of the decrease in pH value of boiler water, and severe corrosion in turbine low-pressure cylinders [5,6]. Thus, the OM entering the water–steam cycle of a

power plant has been considered one of the serious contaminants in the industry [7].

There are many different ways in which OM may get into water–steam cycles [8]. One important pathway is OM brought into the system via the makeup water under standard operation conditions. OM is removed by several units of water treatment, such as coagulation, enhanced coagulation, activated carbon filtration, and membrane technology water treatment. Coagulation is an economical and effective method to remove the suspended and colloidal OM, but the removal rate of dissolved OM is less than 10% [9]. As an adsorption process for removing OM in water, activated carbon filtration is widely employed before deionization, and the stable removal rate of OM is about 40% [10]. The adsorption of activated carbon on the OM depends on its distribution state. Commonly, it has a better effect on the removal of organic compounds with a molecular weight range from 500 to 3000 Da, and has little effect on OM with molecular weight is less than 500 Da or more than 3000 Da [11]. Ion-exchange resin is not used as a means to remove OM, although it is an organic scavenger type in the way of ion exchange and adsorption. OM clogs the mesh of the ion-exchange resin in desalination systems; as a result, the operation capacity of resin decreases and the quality of brine declines [12]. Besides,

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there are electrically neutral fractions of OM which are not effectively removed with any ion exchanger type [13]. Thus, the existing pretreatment and ion-exchange technologies cannot effectively remove dissolved OM, and normal pretreatment methods can only remove approximately 40–60% OM in the water [14,15]. These residues can be removed by membrane treatment such as nanofiltration (NF), and reverse osmosis (RO). The NF can remove OM with molecular weight more than 200 Da, and the OM can be completely separated and discharged out by RO. However, OM in the make-up water can pollute the membrane separation system, which reduces the water permeability and separation performance of membrane [16–19]. In addition, RO is not widely used to remove OM on account of high investment and operating costs. Generally, the TOC concentration of make-up water is in the range of 0.01–0.6 mg/L for the sites where a surface water source is treated conventionally without reverse osmosis.

The role of OM in corrosion is well understood, although its significance is a subject of discussion between boiler operators and manufacturers [20]. Previous researches of the OM in power plant cycle chemistry had emphasized the possible side effects include corrosive degradation products, interference with monitoring cation conductivity, influence on boiling and on condensation, and fouling [21–24]. OM produce volatile acidic degradation products, but the amine provides cations for pH counterbalance. In contrast, the OM also produce inorganic degradation products, but with no ions for counterbalance. Some anions could cause corrosion damage to high-temperature water and thus increase operational risks [25–28]. Zhang et al. found higher chloride concentrations in the waters induced lower corrosion resistance, and the corrosion resistance of steels was also influenced by the concentration of sulfate in the water [29]. Howell hold the view that sulfate contamination in steam can lead to disastrous turbine pitting and corrosion cracking [30]. For this reason, the inorganic decomposition products –chlorine, sulfur, phosphorus, as well as other components in organics, must be considered as potentially corrosive. However, the conventional determination of organics (TOC) only represents the carbon content inorganics, excluding chlorine, sulfur and other more corrosive elements. It is suggested the total organic carbon ion (TOCi) be applied instead of the TOC to evaluate the organics content in water for power plants [31]. And the TOCi represents the content of total carbon in organics and other impurity atoms, which could produce anion after oxidation [1]. Much of the research on OM in power plants in the last two decades has examined the way of OM removal, the measurements of OM, the behavior of OM, and the influence of OM degradation products in power plant cycle chemistry. However, little attention has been focused on the inorganic decomposition products of organics in power plant water-steam cycles. Further studies are still indispensable to provide more dates on the decomposition rates of OM and the contribution ratio on cation conductivity.

In the present study, a series of decomposition experiments were performed in high-temperature water. The contents and components of the samples were analysed with an ion chromatography (IC) system and a total organic carbon (TOC) analyser. This study focuses on the influences of low-molecular-weight organic acids and impurity ions produced from HA decomposition. The influences of various parameters, namely HA concentration, temperature and decomposition time, were determined and discussed.

2. Experiment

2.1. Reagents and solution

The main reagents used in this experiment included sodium hydroxide, hydrochloride, sodium chloride, and sodium sulfate

were all of analytical grade and supplied by Sinopharm Chemical Reagent, Shanghai, China. Humic acid purchased from Aldrich Chemical Co. Ltd. The mass fraction of HA (Sigma–Aldrich, Steinheim, Germany) in the experiment was 81.7%. So the HA was further purified to remove ash by following the procedure described by Nash et al. [32]. And the low-ash humic acid solid was washed with ultra-pure water to remove all anions. Ultra-pure water (18.25 MΩ cm) was prepared with a water purification unit (Zoomwo, Changsha, China). The resulting low-ash humic acid solid was then freeze-dried. The purified humic acid powder was dissolved in a small amount of 0.1 mol L⁻¹ ammonia water, and the humic acid solutions of desired concentrations were prepared by diluting with water [33,34]. The elemental composition of the HA samples includes approximately 30%–60% carbon, 30%–50% oxygen, 4%–5% hydrogen, 1%–4% nitrogen, 1%–2% sulphur and 0–0.3% phosphorus. The principal body of HA is composed of carboxyl and hydroxyl groups instead of aromatic structures. The main functional groups include phenolic hydroxyl, alcohol hydroxyl, carboxyl, hydroxyl, sulfonic acid, amino, quinone and methoxy groups. The sizes of the HA molecules present in water indicate that they are in the colloidal range, and the HA concentration, pH and ionic strength control the colloidal structure [35]. Therefore, no uniform definition of the structure is available at present. The HA hypothetical structure proposed by Schulten [36] is shown in Fig. 1 and the basic unit structure is presented in Fig. 2.

2.2. Experimental equipment and procedure

In the present study, all experiments were performed in autoclaves, as shown in the device diagram in Fig. 3. The experimental system mainly consists of five parts: (1) temperature controller, (2) autoclave reactor, (3) cooling system, (4) sampling system and (5) deaerating system.

We designed the test to simulate all-volatile treatment (oxidation) in the thermal power plant in accordance with DL/T 805.4 ‘Guideline for cycle chemistry in fossil plants – Part 4: Feed water treatment’ [1]. All-volatile treatment (oxidation), which applies only ammonia (or an amine of lower volatility than ammonia), does not use a reducing agent and allows a sufficient oxygen residual to ensure an oxidizing condition. Firstly, 800 mL of the pre-made HA solution with various concentrations (i.e. 1.5, 2.5, 3.5, 4.5, 5.5, 7.5, 10, 15 and 20 mg/L) was added to an autoclave. The pH of the test solution was adjusted within the range of 9.50–9.55 by using ammonia. The pH was measured with a digital pH meter (Hach, Colorado, USA). Next, nitrogen was kept flowing into the autoclave for at least 1 h to blow away the oxygen, and the dissolved oxygen was less than 10 µg/L (ppb). After oxygen removal, the autoclave was tightly closed and heated to the maximum temperature at a set temperature rate. The duration of temperature increase differed at varying temperature rates, and the rising time to the average temperature was approximately 30 min. Once the cell temperature was stable, the designated temperature was maintained for 12 h within a fluctuation range of ±1 °C. As desired, HA was decomposed into various types of products. When the high-temperature heating was completed, the gaseous products were condensed, collected and treated. Then, the power was switched off. Finally, 20 mL of the liquid product was collected from the autoclave after cooling naturally at room temperature.

Two sets of pyrolysis experiments were performed. Firstly, pyrolysis experiments were performed on purified HA solution at different mass concentrations (i.e. 1.5, 2.5, 3.5, 4.5, 5.5, 7.5, 10, 15 and 20 mg/L). Each experiment was conducted for 12 h at 350 °C. Secondly, pyrolysis experiments were performed on the HA solution for different times at 350 °C. The concentration of HA was 7.5 mg/L, which is the average concentration of OM in

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