Research on the On-line Detection Device for Measuring Water Hardness in Industrial Boilers

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Abstract: The hardness of boiler water is a crucial indicator that affects the safe and economic operation of boilers, making accurate and efficient monitoring of it essential. This research project systematically investigates the primary methods for detecting water hardness, delving into their principles, operational procedures, application costs, and accuracy. By integrating the specific environmental factors of industrial boiler applications, the project aims to develop a novel, efficient, and precise method for measuring boiler water hardness. This endeavor provides a theoretical foundation and technical support for the research and development of an on-line detection system for industrial boiler water quality.

Keywords: Water Hardness; Boiler Water; Testing Technique; On-line Detection

1. Introduction

With the relentless advancement of industrial production and the steady growth of the national economy, the deployment of industrial boilers has seen a yearly surge, accompanied by ever-increasing demands for the purity of boiler water. The hardness of boiler water, which refers to the total concentration of calcium and magnesium ions in the water, serves as a vital indicator for assessing boiler water quality. When the hardness of boiler water is excessively high, the solubility of calcium and magnesium ions in water decreases with increasing temperature, leading to the formation of solid deposits composed of substances on heating surfaces with high thermal loads. These deposits, colloquially termed "scale," are composed of substances like calcium carbonate and magnesium hydroxide. Their poor thermal conductivity hinders heat transfer, inflating boiler operational costs. In extreme cases, they can induce deformations and cracks in boilers and pipelines, potentially culminating in explosive incidents and posing grave safety risks [1-15]. Hence, the real-time surveillance and regulation of water hardness in boiler feedwater are of utmost importance. To tackle the intricacies and inefficiencies inherent in conventional water hardness detection techniques, researchers have pioneered a spectrum of technologies, encompassing reagent-based online detection, electrochemical analysis, and semi-micro titration methods. This research endeavor embarks on a systematic exploration of the foremost water hardness detection methods, scrutinizing their applicability, accuracy, and operational ease. It aims to furnish invaluable insights for research and practical applications across related domains. Ultimately, the conception of a novel, efficient, and precise method for assessing boiler water hardness carries immense significance. It lays the theoretical groundwork and technical backbone for the development of an online detection system tailored to industrial boiler water quality, thereby ensuring the boilers' operation remains environmentally friendly, safe, and economically viable.

2. Detection Methods of Water Hardness

Currently, the prevalent practice in boiler water hardness measurement and analysis leans heavily on offline techniques, utilizing a range of methods that encompass chemical, physicochemical, and electrochemical approaches [13-16]. Herein, we present an overview of several widely adopted methods for assessing water hardness in industrial boilers.

(1) Complexometric Titration Method (EDTA Titration Method)

The EDTA titration method is frequently employed for the quantitative analysis and ascertainment of water hardness. It finds widespread application in high-pressure, medium-pressure, and certain low-pressure boilers, as well as in various other contexts where the hardness of water samples must be precisely determined. This method is also the preferred detection technique outlined in the water quality standards for industrial boilers in China. The process entails the gradual addition of EDTA to the water sample being tested, until a complete color transition from purple-red to blue occurs, signaling the endpoint of the titration. By quantifying the amount of EDTA used, one can calculate the total hardness of the water sample. While this method boasts high measurement accuracy, it demands a considerable amount of time and requires operators to be adequately trained and proficient in the procedure. The underlying principle of this determination is elaborated below:

HIn+ Ca(Mg) → Ca In (Mg In) + H

Blue purplish red

NaHY + Ca(Mg) → Na Ca Y(NaMg Y) + 2H

colorless complex

NaH Y + Ca In(Mg In) → NaCa Y(NaMg Y) + HIn+ H

(2) Colorimetric Method

Adjust the pH of the water sample to an optimum level, and then introduce a precisely measured amount of indicator (typically, a blend of suitable reagents proportioned meticulously to craft a specialized hardness colorimetric reagent). Give the mixture a thorough shake. Subsequently, compare the hue of the water sample against the shades on the standard colorimetric plate, and thereby ascertain the range of the water sample's hardness value, enabling a judgment on whether it surpasses the acceptable standard. Generally, facilities utilizing low-pressure boilers lack the capability to prepare and produce hardness colorimetric reagents in-house; hence, they can procure ready-made products available on the market for their use. Among the commonly utilized hardness colorimetric reagents are eriochrome black T, acid chrome blue K, and acid chrome dark blue. This method is solely applicable for the qualitative assessment of water hardness.

(3) Spectrophotometry

This method employs acid chrome blue K as the color-developing agent and incorporates an NH_3-NH_4Cl buffer solution (pH = 10.0) into the process. It then proceeds to plot the absorption spectral curves for the colored complexes formed by calcium ions and magnesium ions, both at equimolar concentrations. The point where these two curves intersect, at a wavelength of 468 nm, signifies the equimolar absorption point for calcium and magnesium ions, which is subsequently adopted as the maximum absorption wavelength. Under optimal conditions, the measurement of the total calcium and magnesium ion content, within a concentration range of 0 to 0.03 mmol/L, adheres to Lambert-Beer's law. This method yields measurement results with an accuracy comparable to that of the EDTA titration method, while also boasting remarkable stability, high sensitivity and precision, cost-effective reagents and instruments, and a straightforward operational procedure. However, it does demand a high level of professional competence from the operators.

(4) Automatic Potentiometry

The disodium ethylenediaminetetraacetate (EDTA-2Na) titration method stands as a prevalent titration analysis technique, extensively utilized for measuring the total hardness of water in contemporary practice. The potentiometric titration approach builds upon the conventional titration method, leveraging the relationship between the activities of calcium and magnesium ions and the potential of the measuring electrode, as governed by the Nernst equation. By monitoring the electrode potential's shift during the titration, the titration endpoint is precisely determined. Automatic potentiometric titration manages the titration process through a programmed sequence, discerns the endpoint with precision, and efficiently handles data processing and result computation. This method boasts rapid testing, straightforward operation, highly accurate and dependable results, and excellent reproducibility. Nonetheless, it does come with considerable equipment and maintenance expenses.

(5) Rapid test strip method

This method is tailored to the factory's actual production needs, employing rapid test strips to detect the total hardness of ingredient water, cleaning water, and source water. Through a comparative analysis with the national standard method, it has been demonstrated that the detection results of this approach are in close agreement, exhibiting no significant disparity. As such, it fully satisfies the water quality detection requirements inherent in the production process. However, it is important to note that this method is specifically suited for water with high hardness and does not align with the water quality standards required for industrial boilers.

(6) On-line Detection Technology

The research on the online detection system of water hardness based on color digital analysis mainly realizes the online automatic testing of water quality hardness through a color sensor. This technology is based on the traditional ethylenediaminetetraacetic acid (EDTA) complexometric titration method and uses the programmable color sensor TCS230 as the core. By combining the measurement and control technology of the single-chip microcomputer, this system can automatically identify and determine the titration end point instead of human eyes, thus realizing the online automatic measurement of the total hardness of water quality.

In addition, through the white balance correction of the color sensor, experiments with different concentrations can be configured to qualitatively analyze the curve trend of the system for detecting water quality hardness. And by comparing the polynomial fitting curves and first derivative curves of different color models, the RGB color model is determined as the color model for end point determination. Such a design not only improves the accuracy and reliability of the color sensor in detecting the color during the titration reaction process, but also realizes the online monitoring of the titration process through serial communication.

The online detection system for the hardness of water used in the once-through steam boiler designed by Chen realizes the rapid and accurate detection of water hardness through a color sensor and an automatic sampling system, significantly improving the efficiency and safety of water quality monitoring [1]. In addition, the automatic online monitoring system for water quality hardness developed by Gong et al., in combination with the upper computer system, realizes high-precision water quality monitoring and management, and significantly improves the economic benefits of water treatment [3].

The research on the online water quality hardness detection system is not limited to Chen Bo's online reagent detection technology. There are also technologies such as the ion selective electrode technology by Li [6] and the research on water quality hardness sensors by Ma et al. [9]. These studies all adopt advanced technologies and methods, such as digital filtering algorithms, digital signal conversion, color sensors, etc., to improve the accuracy of detection and reduce the interference of external factors.

The successful application of these systems not only improves the automation and intelligence level of water quality monitoring, but also provides technical support for realizing remote monitoring and optimizing the water treatment process.

In summary, traditional methods for detecting water hardness have long been a staple in laboratory-based water quality analysis. Yet, they are not without their shortcomings, including the intricacy of their operational procedures, the expense of the required equipment, and the inconvenience of on-site application. Research into online detection equipment, both domestically and internationally, has encountered hurdles such as non-compliance with national standards and inadequate accuracy.

Hence, this research endeavor takes a novel approach, rooted in the reagent colorimetric method. By harnessing the color recognition capabilities of advanced color sensors and integrating them with contemporary electronic and control technologies, it achieves automatic detection and real-time monitoring of water hardness. This innovation offers a fresh technical pathway for the online assessment of water hardness.

3. Online Detection System for Water Hardness

The online detection system for water hardness includes: sampling control system, buffer solution dispensing unit, indicator dispensing unit, stirring system, EDTA titration unit, titration end point determination system, light source, constant volume system, alarm system, waste liquid discharge system, etc.

(1) Select the color-developing agent

Select the color-developing agents such as eriochrome black T, acid chrome blue K, and the mixed indicator of acid chrome blue K-naphthol green B, and carry out the detection of water hardness respectively. It is found that when detecting low hardness, the color change of acid chrome blue K is more obvious. Therefore, acid chrome blue K is selected as the color-developing agent.

(2) Reaction time

The experiment shows that the process of forming complexes between Ca^{2+}, Mg^{2+} and acid chrome blue K can be completed in a very short time and remains stable within 2 hours. Therefore, the titration operation can be completed within 5 minutes after adding the color-developing agent.

(3) Sample temperature

As the temperature climbs, the hue of the reactants gradually fades. The experiment ought to be conducted while maintaining the sample temperature below the 30℃ threshold.

(4) Constant volume system

A micro peristaltic pump is used for quantitative sampling. Through the design of the sampling process and the calculation of the volume of the pipeline, the sampling volume is precisely controlled at 100 mL. An overflow port is set at the upper part of the constant volume container to prevent damage to the electrical components caused by the overflow of the water sample in case of drainage failure or sampling pump failure.

(5) Alarm system

In accordance with the GB/T 1576-2018 "Water Quality for Industrial Boilers" standard and taking into consideration the specific conditions of the enterprise's boilers and water treatment facilities, an alarm threshold shall be established. Should the hardness detection reveal any exceedance of the standard, an alarm shall be promptly triggered to alert the operators, enabling them to address the issue scientifically and prevent feed water with excessive hardness from infiltrating the boiler system.

(6) Liquid Addition Unit

The EDTA titration unit demands an exceptionally precise dropping volume, accurate to 0.01 mL. To meet this requirement, a peristaltic pump of minimal volume and superior precision should be chosen, ensuring accurate detection of water samples with even the lowest levels of hardness.

(7) Endpoint Determination Unit

A color sensor is employed to pinpoint the color at the point of abrupt change and the color that corresponds to the alarm threshold, with these hues being stored as benchmark colors. Throughout the detection process, the hardness of the water sample is determined by monitoring the color transformation, thereby achieving the objective of real-time online detection.

4. Conclusions and Prospects

The online hardness detection system tackles the intricacies and inefficiencies inherent in conventional water hardness detection methods. By diminishing reliance on personnel and enabling instantaneous monitoring of water quality, it facilitates scientific management of boiler water quality. This, in turn, helps to mitigate potential issues arising from excessive water hardness, including boiler scaling, corrosion, and the looming risk of pipe bursting.

As science and technology advance and environmental protection requirements escalate, the field of water hardness detection technology encounters fresh opportunities for growth alongside formidable challenges. Current research endeavors primarily revolve around the design and implementation of online detection systems, electrochemical analysis techniques, semi-micro titration methodologies, and the exploration of water hardness sensor performance. These studies unveil a spectrum of distinct water hardness detection approaches, encompassing online reagent-based monitoring, electrochemical analysis, titration techniques, and sensor technologies, each with its unique merits and constraints. For instance, online reagent detection systems facilitate real-time surveillance, electrochemical methods boast high sensitivity and selectivity, semi-micro titration reduces reagent expenses and workload, and water hardness sensors offer swift and convenient detection solutions. The integration of a PLC-based control system, as researched by Jiang and Liu, heralds a novel approach to the automation and intelligence of water hardness monitoring. Furthermore, the research and development of innovative sensors by Ma et al., coupled with advancements in electrochemical analysis methods by Sun, pave the way for enhanced sensitivity and accuracy in detection technology. Lastly, the application of the semi-micro titration method proposed by Zhao and Liu not only curtails costs but also champions a more economical and eco-friendly approach to water quality detection.

The future trajectory of water hardness detection technology promises a path towards heightened automation, reduced costs, streamlined operation, and unparalleled detection sensitivity. Alongside these advancements, there will be a heightened emphasis on environmental stewardship and human wellbeing. By delving into and refining sensor technology, we can elevate the response speed and measurement precision of water hardness detection. Machine learning and artificial intelligence algorithms will be harnessed to refine data analysis, thereby enhancing the data processing prowess and accuracy of detection systems. Furthermore, the creation of more cost-effective and eco-friendly reagents and consumables will catalyze the widespread adoption of these technologies across a broader array of application domains.

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