

A Real-time Corrosion Monitoring Method Based on Quartz Crystal Microbalance

Chaoxuan Qin^{1,*}, Lu Dai¹, Yuqin Zhu¹

¹ Southwest Technology and Engineering Research Institute, 401329 Chongqing, China

Abstract. This paper put forward a kind of fast, high precision, high sensitivity of corrosion monitoring method and developed a portable corrosion monitoring device with 6 road crystal vibration sensor and a temperature and humidity based on QCM theory. The device can work independently for a long time in harsh outdoor environment without relying on external power supply. The quantitative relationship between quartz crystal vibration frequency and corrosion quality was determined by calibration tests in the laboratory. The device is placed in a certain environment to monitor the corrosion. The results show that the device can effectively monitor the weak corrosion phenomenon, with real-time and high sensitivity.

1 Introduction

Metal is one of the most important materials for industrial equipment. In the process of service, metals are prone to corrosion under the action of environment and corrosive medium, the equipment is easy to form thinning, mechanical performance reduction, cracking, punch, etc., leading to equipment failure and safe hidden trouble, cause environmental pollution, and may even bring huge economic losses or safety accident. So, it is very important to monitor, prevent and warn the corrosion. At present, the main corrosion monitoring methods include metal hanging sheet method and resistance probe method, etc. These methods can only monitor uniform corrosion, and will destroy the integrity of the equipment itself during installation. Quartz Crystal Microbalance (QCM) is a new type of mass sensing and analysis technology with nanogram sensitivity[1]. It can reflect the mass change of adsorbable substance on the crystal surface by monitoring the resonant frequency change of quartz crystal. It has the advantages of high sensitivity, and real-time monitoring. QCM as a kind of high precision, high accuracy of the testing instrument is widely used in chemical, biological medicine, food, aerospace and other fields.

Corrosion monitoring is a hot research topic. The physical approach is to assess the corrosion of rebar by detecting changes in physical properties, including resistance, electromagnetism, heat conduction and sound propagation. These methods include time domain reflectometry (TDR)[2], X-ray diffraction and atomic absorption probe techniques, infrared (IR) thermography[3], and fiber corrosion detection[4]. Based on the modal analysis theory of elastic materials, Chen et al[5]. established a modal analysis model for corroded pipes and analyzed the relationship between the modes of corroded pipes and quality loss factors. The results show

that the model can be used to evaluate the corrosion rate of corroded pipelines by monitoring and analyzing the modes. Dai [6] conducted in situ simulations using the HYSYS program to study the effects of operating conditions, inhibitors, pipeline parameters and flow modes on CO₂ corrosion in order to predict CO₂ corrosion in natural gas collection pipeline systems. The study showed that the corrosion rate was influenced by working pressure and carbonate concentration, and that there was an optimal value for the promotion of corrosion by temperature. By comparing the simulation data with the corrosion rate data in the field, the feasibility of the numerical simulation method is proved.

Based on QCM technology, a portable corrosion quality monitoring device is developed in this paper, which provides an efficient method for online corrosion monitoring and real-time early warning.

2 QCM theory

QCM [7] works by applying an alternating electric field through two electrodes to a quartz wafer, which is subjected to periodic mechanical deformation due to the inverse piezoelectric effect. This mechanical vibration propagates from the wafer in the form of thickness shear sound waves, known as thickness shear (TSM) oscillations. Generally speaking, the amplitude of this mechanical vibration is very small, but when the frequency of the alternating electric field is a certain value, the amplitude will suddenly increase, resulting in resonance, that is, piezoelectric oscillation.[8]

Under the alternating electric field, QCM generates a shear wave of a certain wavelength due to the piezoelectric effect. The shear wave propagates in the crystal along the direction parallel to the alternating electric field and is completely reflected at the crystal

* Corresponding author: qinchaoxuan1991@163.com

interface, that is, it generates a standing wave.[9] The conditions are as follows:

$$h_q = n\lambda_0 / 2 \tag{1}$$

Where h_q is the thickness of the quartz crystal oscillator and λ_0 is the shear wave length.

Assuming that the properties of QCM[10] surface material are similar to QCM -- and uniformly attached to QCM surface, the relation between frequency change and thickness change can be obtained by setting its thickness as Δh :

$$\Delta f = -\frac{\Delta m}{A\rho_q h_q} f_0 = -\frac{\Delta m}{A\rho_q h_q} \frac{f_0^2}{\frac{1}{2h_q} \sqrt{\frac{u_q}{\rho_q}}} \tag{2}$$

There are the following restrictions: (1) the frequency offset should be within 2% of the fundamental frequency; (2) The material on QCM surface is evenly distributed; (3) The crystal works in a resonant state.

According to Sauerbery's equation, when a QCM sensor plated with metal electrodes is working, the metal electrode will be corroded by corrosive gases in the air, resulting in an increase in the surface mass of the QCM sensor. The increase in mass Δm can be calculated from the output frequency change of the QCM sensor Δf . Then according to the corrosion time and the area of the metal electrode, the metal corrosion rate can be calculated.[11] The crystal oscillator structure used in this paper is shown in Fig. 1. There are metal coatings on both sides of the quartz sheet, and the metal coatings are connected to the pins through the electrodes. The crystal vibrates steadily when a specific voltage is applied to both ends of the electrode. When the metal coating is exposed to the environment, corrosion will occur under the influence of the environment, and then the quality of the metal film will change, and the frequency of crystal vibration will change accordingly. By measuring the frequency of vibration, the corrosion of the metal can be monitored.

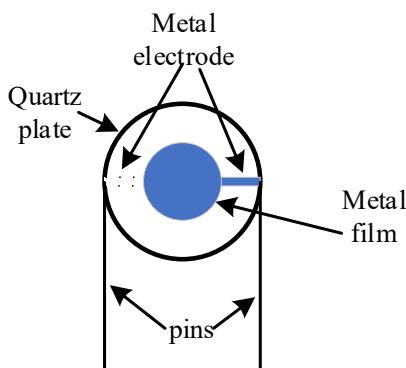


Figure 1. structure of quartz crystal

3 Portable corrosion monitoring device

Based on QCM principle, the corrosion test device was designed, its structure is shown in Fig. 2, the device is the core of the circuit by epoxy potting process, through the large capacity polymer lithium battery for power supply,

makes the device work normally in harsh outdoor environment, through the low power design allows the device to get longer working hours. Each crystal oscillator is connected to a resonant circuit, through which the crystal oscillator generates stable vibration, and the vibration signal is transmitted to the main control circuit. The calibration and conversion algorithm of QCM is realized in the main control circuit, which measures the frequency of vibration and converts the frequency into corrosion weight gain or weight loss. The clock source provides the running clock for the master circuit. The temperature and humidity sensor collects the ambient temperature and humidity, and compensates the temperature and humidity through the main control circuit to improve the test accuracy and make up for the drift caused by the temperature and humidity. The measurement results of the main control circuit are stored in the flash memory chip. Through the upper computer can read and display the measured data.

Fig 3. is the physical picture of the device. There is a temperature and humidity sensor and 6 quartz crystals at the top, which are removable and replaceable. When not working, protective covers can be installed for protection. The working indicator light displays the working state of the device. When the corresponding sensor is working, the indicator light will blink, and the power indicator light displays the remaining power of the device.

Device installation program flow chart as shown in Fig 4., after work, first of all determine whether need to transmit the data to upper computer, after the initialized clock, timer, flash, etc, when reach the setting of sampling time, began to each sensor data acquisition and calculation during the frequency writing flash, after quality of converting frequency to corrosion.

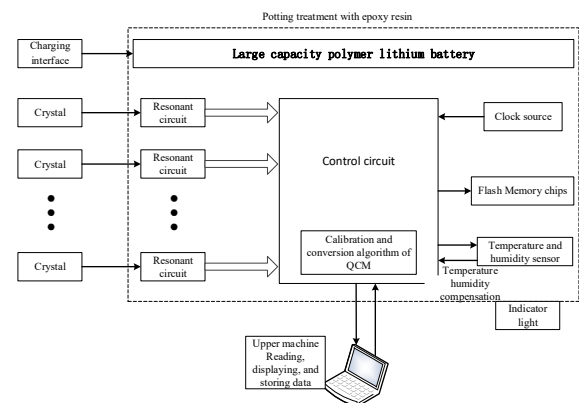


Figure 2. Structural composition diagram of the corrosion test device

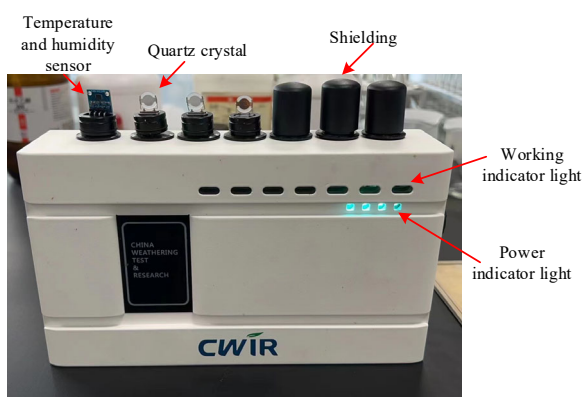


Figure 3. Real figure of the corrosion test device

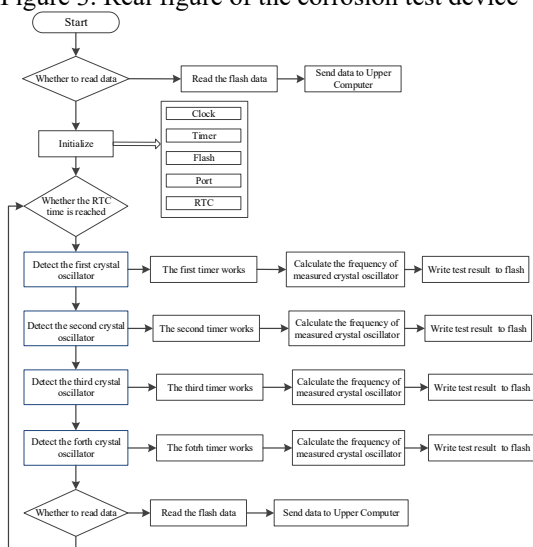


Figure 4 Program flow chart of the corrosion test device

4 Experiment

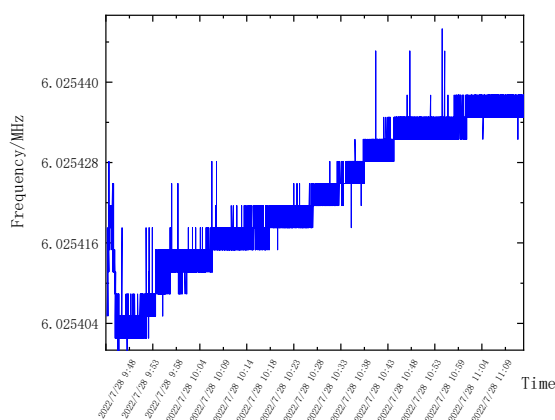


Figure 5 Corrosion test results

A large number of calibration tests were carried out in the laboratory. The relationship between frequency change and corrosion quality change was obtained by using AgNO_3 , KCl and Na_2SO_4 solutions for solution calibration experiments in the laboratory. Finally, the relationship was obtained as follows:

$$\Delta m = \Delta f / 644.2 \quad (3)$$

To test the corrosion monitoring effectiveness of the device, place the device under the environment of a corrosion monitoring, the result is shown in Fig. 5, the curve shows an hour or so of the frequency change, by type 1 can be calculated at this time of corrosion quality 0.056 ug, traditional methods are difficult to corrosion status of monitoring to the product in a short time, and the method can real-time monitor the corrosion condition, It has extremely high sensitivity.

5 Conclusion

To solve the real-time monitoring for corrosion problems, in this paper, based on the QCM design principle, put forward a kind of fast, high precision, high sensitivity of corrosion monitoring method and developed a portable corrosion monitoring device with 6 road crystal vibration sensor and a temperature and humidity. The device can work independently for a long time in harsh outdoor environment without relying on external power supply. The quantitative relationship between quartz crystal vibration frequency and corrosion quality was determined by calibration tests in the laboratory. The device is placed in a certain environment to monitor the corrosion. The results show that the device can effectively monitor the weak corrosion phenomenon, with real-time and high sensitivity.

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