Electrochemical Noise Analysis of 20# Steel with Different pH Value in Sodium Chloride Solution

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Abstract. The corrosion behavior of 20# steel in sodium chloride solution with different pH value has been studied by the electrochemical noise (EN) technique. The EN data was analyzed using methods of the frequency-domain, time-domain and wavelet analysis. The result show that the Cl- in the solution for high pH value effect local corrosion process at the matrix that caused the difference spectrum of electrochemical noise analysis. With the high pH value condition, localized corrosion was occurred for Cl- in the early stage of the experiment mainly. For the pH value decreased, uniform corrosion of H+ was in a dominant position on the substrate, When pH reached 3, due to H+ concentration is larger, greatly promoted the activity of Cl-, therefore, there was some localized corrosion happened in the middle of the experiment. The wavelet analysis show that different bands correspond to different corrosion behavior and the result is consistent with the conclusion of others analysis method.

1. Introduction
Metal corrosion is an electrochemical process, which is due to the metal material to reacts with the external environment and makes its property deterioration [1]. When the metal is exposed to the electrolyte, the anode of metal lose electrons, the electrons is absorbed by cathode. At present, there are many techniques used to monitor the corrosion process, these techniques can be divided into disturbed or undisturbed, directly or indirectly [2, 3]. Monitoring with disturbance applied an additional test signal to the system and measure corrosion parameters, such as electrochemical impedance techniques, linear polarization techniques. The indirect corrosion monitoring techniques only measure the final result of corrosion, Such as ultrasonic thickness measurement, imaging techniques. Electrochemical noise technique as a direct measurement without disturbance technology has proven to study the corrosion process proved is very effective [3-10]. Electrochemical noise is defined as the process of corrosion potential and current random fluctuations, the fluctuation is considered to be a reflection of the essence of the corrosion reaction. This method is simple and without disturbance on the corrosion system which can be widely used in theoretical research and industrial corrosion monitoring.

The essence of Wavelet transform is the filtering process for original signal. The signal is projected into the subspace which consisting of a set of mutually orthogonal wavelet function, unfold the formation of the signal in different scales. For frequency spectrum analysis, wavelet transform is decomposed into low and high frequency to signal frequency, in the next stage transformation, the low frequency part is decomposed into more low frequency and high frequency again, and so on, then finished at a deeper level of wavelet decomposition.
2. Experimental

2.1. Experimental experiment
The CS350 electrochemical workstation was used to measure the electrochemical signal, which was made by Wuhan Corrtest instrument Co.

2.2. Experimental procedures
The 20# steel prepared into the size of 10×10×3mm³, one side of the sample welding copper wires, leaving side as the working electrode surface (area of 1cm²), the rest of the sealed with epoxy resin. Before the experiment, the electrode surface is grinded by 1000 # waterproof metallographic sandpaper, polishing, rinse with acetone, wipe dry. Corrosive medium is the mass fraction of 3.5% NaCl in de-ionized water. Chemical reagents used analytical reagents.

2.3. Electrochemical noise measurement
Using CS350 zero resistance current modules (ZRA) measure the current and the potential noise simultaneously at open circuit potential in system. Test system using the three-electrode system, two identical N80 electrode as working electrode (working electrode 1 and working electrode 2), saturated calomel electrode as the reference electrode. The electrochemical current noise was measured as the galvanic coupling current between two identical working electrodes (WE) kept at the same potential. Sampling interval is 0.5s; the sampling frequency is 2Hz, 4096s as a test cycle. Experimental total duration is 15872s, a total of four test cycles to experimental data text. The data were recorded immediately after the immersion of the working electrodes in the solution. Experiments under room temperature (20±2°C) carried the entire electrode system in a Faraday cage for make electromagnetic shielding

3. Results and discussion

3.1. Time-domain spectrum

3.1.1. Electrochemical noise pH=7 solution. Electrochemical current noise was measured 60h in the pH=7 solution as shown in figure 1 for current noise verse time spectrum. At the early stage the presence of substantial fluctuations was shown in the time-current spectrums. With the experiment precede the current noise become smooth and reduce the fluctuation in the late of the experiment. All of the data was shown that it was dominant for the DC offset in spectrum; the larger of the vibration amplitude for DC offset submerged the details of the corrosion signal from electrode surface. Therefore, the original spectrum was unable to reflect the corrosion of the sample, so it was necessary to remove the DC drift noise from the original signal.

![Figure 1. Original electrochemical current noise spectrum in the pH=7 solution](image_url)
The above original signal was removed DC drift below maps by 9 order wavelet method, as shown in Figure 2. As seen from the spectrum, the amplitude of electrochemical noise was of in the vicinity of $1 \times 10^{-7}$ A, and fluctuation of it was more even with except to two vibration reach $1 \times 10^{-6}$ A greatly, therefore it was characteristics of uniform corrosion. One of the fluctuations was shown at the beginning of the experiment, another at the middle of the experiment, and then at the end of the experiment some small fluctuation was shown. It was indicated that at the pH=7 solution there was domain of the uniform corrosion, but at some stage, it was also shown local corrosion for the Cl- in the solution.

3.1.2. Electrochemical noise pH=5 solution

As seen from the spectrum, the amplitude of electrochemical noise was reached $2.1 \times 10^{-8}$ A, all amplitude are relatively uniform, and the balance of positive and negative amplitudes satisfied the Gaussian distribution, which is characterized by uniform corrosion. From figure 2, the vibration frequency is larger than the figure 4, indicated that the corrosion event frequency is intensified.
3.1.3. Electrochemical noise pH=3 solution

![Figure 5. Original electrochemical current noise spectrum in the pH=3 solution](image)

![Figure 6. After removal of the DC drift electrochemical noise spectrum in pH=3 solution (a) After removal of the DC drift electrochemical noise spectrum in pH=3 solution (b) Enlarged of (a)](image)

Electrochemical current noise was measured 60h in the pH=3 solution as shown in figure 5 for current noise verse time spectrum. From the spectrum can be seen, the DC offset temporarily in the dominant position, from the macro view, the vibration corrosion of the figure 5 is the weakest of figure 1 and figure 3, but also DC offset flooded to reflect details the signal of electrode surface state. The above original signal was removed DC drift below maps by 9 order wavelet method, as shown in Figure 6.

Seen from the spectrum, the middle part has an obvious amplitude intensified, the amplitude of vibration is $4 \times 10^{-7}$A, the rest amplitude are uniform. The noise amplitude basically reached $2.1 \times 10^{-8}$A, and the balance of positive and negative amplitudes satisfied the Gaussian distribution, which is characterized by uniform corrosion.

Discovered from the time-domain spectrum comparison, in the case of pH decreases, H+ concentration of the solution will increase, the role of 20# steel’s corrosion is more obvious. In the high pH value condition, Cl- induced localized corrosion mainly in the early stage of the experiment, there is obvious amplitude. pH value decreased, uniform corrosion of H+ has taken on the substrate material, at the same time combined with the local corrosion of Cl-. When pH reached 3, due to H+ concentration is larger, greatly promoted the activity of Cl-, therefore, there was some shock wave shape of localized corrosion in the middle.

3.2. Frequency domain

Above the noise - time spectrum was used Fourier transform to get frequency domain curve, as shown in the figure below. The pH = 7 is significantly higher than pH = 5 and pH = 3 results. The corrosion of pH = 7 show that there are differences with the others. This is similar to the previous discussion, appeared the localized corrosion. From the figure can be seen with increasing frequency, frequency domain appears more substantial fluctuations, due to the high frequency data noise corrosion signals mixed various noise
signal. Individual abnormal fluctuations appear at high frequencies of PH = 3. This indicates that the uniform corrosion process also appeared the localized corrosion noise signal.

![Graph](image1)

**Figure 7.** Frequency-domain map of the electrochemical noise (a) pH=7 (b) pH=5 (c) pH=3

### 3.3. Wavelet analysis

![Graph](image2)

**Figure 8.** Wavelet analysis map of the electrochemical noise (a) pH=7 (b) pH=5 (c) pH=3

Wavelet analysis results are shown in figure 8. From the figure can be found d1-d6 band appeared significant local fluctuations at pH = 7, mainly to noise signal intensity fluctuate at pH=5 and pH=3 corresponding band.

The d1-d4 curve of pH=7 spectrum is different from it of pH=3 and pH=5. The pH=7 curve show the periodic fluctuation, while it of pH=3 and pH=5 showed a more irregular changes and fluctuations. All d4-d13 band of the spectrum is similar. Some researcher have pointed out that d1 ~ d3 band of the
current noise represent adsorption process or anodic dissolution process, d4~d7 band represents the local corrosion development process, d8~d9 band show diffusion process. The analysis results show that, the anodic surface dissolution controlled the process of corrosion; and the degree of diffusion effect increasing with the corrosion time slightly strengthened, which has close relationship with the corrosion process. For this experiment, the Cl- in the solution for high pH value effect local corrosion process at the matrix that caused the difference spectrum of wavelet analysis as mentioned before.

4. Conclusion
The result of data show that the Cl- in the solution for high pH value effect local corrosion process at the matrix that caused the difference spectrum of electrochemical noise analysis. With the high pH value condition, localized corrosion was occurred for Cl- in the early stage of the experiment mainly. For the pH value decreased, uniform corrosion of H+ was in a dominant position on the substrate, When pH reached 3, due to H+ concentration is larger, greatly promoted the activity of Cl-, therefore, there was some localized corrosion happened in the middle of the experiment.

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