The effect of metakaolin on the hardening process of alkali activated slag by using electrochemical impedance spectroscopy

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Abstract. The purpose of this research work is to study the hardening behavior of the alkali activated slag-metakaolin (AASM) material from a new electrochemical perspective. The measurements of the compressive strength and the electrochemical impedance spectroscopy (EIS) were conducted. The results demonstrated that the strength of AASM paste decreases with the increase of metakaolin content. In addition, a suitable electrochemical equivalent model has been used in order to analyse of the relationship between the microstructure of the AASM paste and the EIS data. And found that the resistance of ion transport process Rct1 show an increasing trend over the testing period and the compressive strength and the Rct1 of AASM has similar growth trend and strong correlation, which means that the EIS may be used to predict the strength development of the AASM paste.

1. Introduction
Mainly due to the low energy consumption, high strength and good durability, AASM materia have attracted widespread interest in the academic research community [1]. So far, research into the development of alkali-activated cementitious materials has shown that this binder exhibits great potential to be an advanced green building material. [2].

In order to better evaluate in a comprehensively way the properties of the AASM material, it is necessary to have a deep understanding of its hardening reaction and its microstructure. In previous researches, a variety of test methods, including: the scanning electron microscopy (SEM), the X-ray diffraction analysis (XRD), and so on, have been applied to the study of the hardening process in order to better understand the chemical and physical mechanisms involved in the development of the strength of the AASM. However, most of them need to pretreat the tested material first, which is destructive. In recent years, the technology of the EIS, a non-destructive method, has been applied on the study of the Portland cement by the researchers, which reveals that this technical method is highly-sensitive to the changes in the microstructure of the materials [3,4]. McCarter et al. [3] first used the EIS to the performance of cement-based materials. This study showed that EIS can effectively monitor the early hydration process of cement. The effect of adding silica fume on the impedance characteristics of the hydrated cement was studied by Gu et al. [4]. The finding demonstrated that the impedance
measurements are very sensitive to changes in hydration kinetics and EIS proved to be a useful tool for testing pore structure in cement systems. Although a few researchers have applied EIS to the research of the alkali activated materials [5], very few detailed studies have been reported and they rarely used the equivalent circuit model to quantitatively analyzed the EIS results. The objective of this research is to use EIS combined with traditional test method to study the hardening reaction characteristics of the AASM. Through the establishment of a suitable equivalent circuit model to analyze the changes of the circuit parameters, by exploring the quantitative relationship between the mechanical properties of the AASM and the EIS performance, thus providing a different window for further research on the microstructure and properties of the AASM.

2. Materials and experiments

2.1. The preparation of alkali activated slag-metakaolin
The sample of the AASM is made of slag and metakaolin (produced in Guangdong Province, China; the chemical composition analysis is plotted in Table 1) and sodium silicate (produced in Guangdong Province, China; 26.00 wt. % SiO₂, 13.76 wt. % Na₂O, 60.24 wt. % H₂O, and a molar ratio for SiO₂/Na₂O of 1.95). The water-solid ratio is 0.35. The metakaolin contents ranging from 0 to 40% with an interval of 10%. The mixture was cast into two different moulds (40 × 40 × 160 mm and 30 × 30 × 30 mm). The previous sample was used for the compressive strength test, and the latter was used for EIS test. The paste specimens were placed in a curing chamber (75 ± 5% RH, 25 ± 2 °C) for 24 hours. After 24 hours, the specimens were demolded and then returned under the same curing chamber until the specimens were tested.

Table 1. Chemical analysis of the slag and metakaolin used in this study using X-ray fluorescence spectrometry (XRF) (wt. %)

|        | CaO | SiO₂ | Al₂O₃ | MgO | SO₃ | TiO₂ | K₂O | Fe₂O₃ | MnO | Na₂O |
|--------|-----|------|-------|-----|-----|------|-----|-------|-----|------|
| Slag   | 41.5| 32.6 | 14.7  | 6.48| 2.48| 0.58 | 0.39| 0.35  | 0.29| 0.25 |
| Metakaolin | 0.19| 49.67| 42.54 | 0.14| -   | 0.18 | 2.14| 1.32  | -   | 0.68 |

2.2. Testing procedure
2.2.1 The electrochemical impedance spectroscopy test. The electrochemical properties of AASM was measured by means of EIS (PARSTAT 4000+, Ametek, USA). The specimens cured for 1 day, 3 days, 7 days, 14 days and 28 days were carried out for the electrical impedance measurement and six samples for each type were prepared for the test. The shematic diagram of EIS test sample is shown in Fig. 1. The EIS measurements were run in the frequency range of 100 Hz to 10 MHz.

Fig 1. The shematic diagram of EIS test sample
2.2.2 **The compressive strength test.** To examine the mechanical properties of AASM paste, the compressive strength test was conducted. The specimens were tested at 1 day, 3 days, 7 days, 14 days and 28 days. The compressive strength measurements with a sample size of $40 \times 40 \times 40$ mm were conducted at a loading rate of 2.4 kN/s. The strength test was in compliance with the standard of GBT 17671-1999 (ISO method).

3. **Results and Discussion**

3.1. **The compressive strength curve of alkali activated slag-metakaolin**

The compressive properties of the AASM paste specimens at different ages are plotted in Fig 2. As expected, the compressive strength of the AASM increased with the age of curing. More specifically, the 7-day compressive strength of AASM can reach over 85% of its 28-day compressive strength, indicated that AASM materials have the characteristics of faster hardening rate in the early stage. In this study, it was found that the strength of AASM paste decreases with the increase of metakaolin content. These results are consistent with other studies [6, 7] and indicate that the strength increases with the increase of calcium (slag content), which is due to calcium dissolution and C-A-S-H gel precipitation. The formation of C-A-S-H gel may provide a driving force for accelerating chemical reaction, reducing porosity, with consequent increase the mechanical strength [7].

![Fig 2. The compressive strength curve of alkali-activated slag-metakaolin](image)

3.2. **The result of the EIS tests**

The Nyquist curve of different hardening times of the AASM is shown in Fig. 3. In the Nyquist plots, it can be seen that the high frequency area is a semicircle and low frequency phase exhibits a straight line at 45° to the horizontal. As the age increases, the diameter of the semicircle becomes larger and larger. The larger semicircle diameter means that the bulk resistance of the sample is relatively large [8]. As can be seen from Fig. 3, during the testing period, the bulk resistance of the AASM paste increased with the age of curing. It can be suggested that, as the age increases, the pore solution ions continue to be consumed to produce hardened products and fill the pore structure, the degree of blocking of the internal interconnecting pores increases, the porosity of the interconnected pores decreases, and the degree of denseness of the microstructure increases [9]. These factors directly makes ion transfer more and more difficult, which in turn leads to the increase of high-frequency semicircle diameter with the curing age.
3.3. The relationship between mechanical properties and parameters using equivalent model fitting

In order to more quantitatively analyze the relationship between EIS experiment and the hardening time, two equivalent circuit models were used to simulate the result of the EIS. Fig. 4 depicts a classical equivalent circuit which is commonly used in the simple electrochemical system. This equivalent circuit model is described as \( R_s(Q(R_{ct}W)) \) according to the Circuit Description Code. Another equivalent circuit, which was proposed by Dong et al. [10], is shown in Fig. 5. This equivalent circuit model is described as \( R_s(Q_1(R_{ct1}W_1))(Q_2(R_{ct2}W_2)) \). The comparison of the measured results of the AASM simulated by two equivalent circuit models is shown in Fig. 6. It can be obtained that the model of the \( R_s(Q_1(R_{ct1}W_1))(Q_2(R_{ct2}W_2)) \) is more matched with experimental points than the model of the \( R_s(Q(R_{ct}W)) \), so this study used the model of \( R_s(Q_1(R_{ct1}W_1))(Q_2(R_{ct2}W_2)) \) to monitor changes in the hardening process of the AASM paste.

![Fig 3. The Nyquist curve of AASM at various ages (metakaolin content: 20%)](image)

![Fig 4. The equivalent circuit of classical electrochemical system.](image)

![Fig 5. The equivalent circuit proposed by Dong et al. [10].](image)
For this study, the parameter of the Rct1 was used to estimate the changes in the porous microstructure of the AASM paste. The Rct1 can represent the resistance of the charge transfer reaction of the hydration electrons, which is inversely proportional to the number of hydrated electrons that can undergo the electrochemical reaction in the internal structure of the AASM paste [11]. It can also reflect the degree of the hardening reaction of the paste. By using the model of $R_s(Q_1(R_{ct1}W_1))(Q_2(R_{ct2}W_2))$ to simulate the EIS test results with different metakaolin contents at different ages, the values of parameter of Rct1 is obtained, as shown in Table 2. It can be seen that, at the same age, the Rct1 value decreases with the increase of metakaolin content, and the Rct1 value of the same sample increases with the extension of curing age. What’s more, a linear relationship between the compressive strength and the Rct1 value for AASM paste was found, as shown in Fig. 7. All correlation coefficients R2 were greater than 0.93, indicating that the correlation between compressive strength and Rct1 values is strong. Therefore, it is reasonable to envision that EIS can be expanded to predict the 28th strength development process in AASM materials.

**Table 2.** Rct1 value of AASM paste with different curing age

| Rct1 | 1d   | 3d   | 7d   | 14d  | 28d  |
|------|------|------|------|------|------|
| 0    | 3103 | 5935 | 8192 | 9399 | 10980|
| 10%  | 779  | 2393 | 4405 | 5002 | 6017 |
| 20%  | 588  | 1697 | 3194 | 3796 | 4337 |
| 30%  | 480  | 1514 | 2576 | 3300 | 3813 |
| 40%  | 395  | 1403 | 2265 | 2893 | 3204 |
Fig 7. The relationship between the compressive strength and Rct1 values for AASM

4. Conclusion
From the experimental data obtained, the following conclusions can be drawn:

The AASM material has a rapid-early reaction rate, the strength of the seven days can reach more than 85% of its 28-day strength. At the same curing age, the higher the content of metakaolin, the lower the strength of AASM.

In the EIS test, with the increase of the curing age, the material continuously produce hardened products and fill in the pore structure, which results an increase in the compactness of the microstructure. These factors directly make the AC signal transmission more and more difficult, which in turn leads to a growth in the diameter of the high frequency semicircle of the AASM.

In comparison to the classical equivalent circuit model, the simulation results of the Rs(Q1(Rct1W1))(Q2(Rct2W2)) model are more closely matched with the experimental results. In addition, it was found that there is a strong correlation between the Rct1 value and the compressive strength, and that correlation coefficient in each case is greater than 0.93. This indicates that the EIS can be used to predict the strength development of the AASM within 28 days.

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