Study on Hydration Behavior of Cement Mortar with Nano-Metakaoline by Electrochemical Impedance Spectroscopy

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Abstract. The hydration process of cement mortar with nano-metakaolin (NMK) for three contents (3%, 5%, 7%) in early hydration stage and stable hydration stage were investigated by electrochemical impedance spectroscopy (EIS). The results show that the addition of NMK can accelerate the hydration process of cement mortar with NMK in hydration early stage (1-12h) and stable hydration stage (1-28d). NMK can increase the resistance of continuous conductive path R_{CCP}. At 28d, the R_{CCP} of specimen with NMK contents of 3%, 5%, 7% were increased by 28.7%, 43.4% and 71.1%.

1. Introduction
Nano-metakaolin (NMK) is made from kaolin (Al2O3·2SiO2·H2O) by dehydration, decomposition and smash at a proper temperature (600-900 °C). NMK is white powder, it’s main components are amorphous silica and alumina[1]. At present, the research on the durability of cement-based with NMK has made some achievements. The results show that NMK can improve the frost resistance[2], chloride resistance[3] and Acid rain resistance[4] of cement-based materials.

The hydration process of NMK cement-based material is the formative process of its durability, therefore, It is very important to study the influence of NMK on the hydration process of cement-based materials. At present, the research on the hydration process of cement-based materials mainly includes X-ray diffraction (XRD), differential scanning calorimetry (DSC-TG), hydration heat method[5-6]. XRD and DSC-TG can analyze the hydration process of cement-based materials qualitatively and quantitatively, but before the test, it is necessary to break, dry and grind the samples at the test age, it's a complex process. The hydration heat reaction is the relationship between heat release and time, and it can also reflect the relationship between hydration degree and time to a certain extent. However, when the cement hydration enters into the stable period, the heat release will be greatly reduced, which will increase the measurement error. Therefore, this method is only suitable for studying the hydration process of cement-based materials in the early stage. Electrical impedance spectroscopy (EIS) is a non-destructive testing method. EIS can be used to characterize the change of internal structure in the hydration process of cement-based materials, and monitor the hydration process of cement-based materials without damage[7]. At present, there are few studies on the hydration process of NMK cement-based materials, and there is no report on the application of EIS to the study of the hydration process of NMK cement-based materials.

In this paper, the EIS of NMK cement mortar in the process of hydration is studied. The EIS characteristics of nmk cement mortar with different dosage and age are analyzed. The influence of
NMK on the hydration process and pore structure of cement mortar is analyzed.

2. Materials and method

2.1 Raw materials
Cement is P.O 42.5R ordinary portland cement produced in Dalian, China. The chemical composition of cement is shown in table 1. NMK is produced in Lingshou County, Hebei Province, China. The chemical composition of cement is shown in table 2. The morphology and XRD pattern of NMK are shown in figure 1.

| Table 1 Chemical composition of cement % (by mass) |
|-----------------------------------------------|
| CaO  SiO2  Al2O3  Fe2O3  MgO  SO3  Llo |
| 59.30  21.91  6.27  3.78  1.64  2.41  4.69 |

| Table 2 Chemical composition of NMK % (by mass) |
|-----------------------------------------------|
| SiO2  Al2O3  CaO  TiO2  Na2O  MgO  Fe2O3  K2O |
| 49.82  44.80  0.28  0.02  1.16  2.23  0.30  0.58 |

![Figure 1 TEM micrograph and XRD spectra of NMK](image)

2.2 Specimens preparation
In this experiment, the equivalent substitution method is adopted, and three NMK contents are used: 3%, 5%, 7%. Corresponding test piece numbers are NMK3, NMK5 and NMK7, and NMK0 is ordinary cement mortar. The water cement ratio of cement mortar is 0.4, and the cement sand ratio is 2:3. Refer to the ‘Test methods of cement and concrete for highway engineering’ (JTG E30-2005) [8] for sample preparation. To achieve a good dispersion of the clay in mortars and mortars, the NMK was first dispersed in water in a rotary mixer at high speed for 15 mins. The inner wall size of the mould used for preparing the sample is 40mm×40mm×40mm, the material of mould is ABS insulating plastic. Two mirror stainless steel electrodes (155mm × 40mm × 1mm) were mortard on the inner side of the mold. After the specimen was formed for 12h, the specimen and mould were cured in the standard curing condition (at a temperature of 20±3℃ and a relative humidity of 95%) until test age.

2.3 Electrochemical impedance spectroscopy measurement
Bio-logic VMP3 electrochemical workstation was selected for EIS test, a three electrodes system was aploited. The counter electrode and the reference electrode were connected to the same electrode plate, the working electrode was connected to another electrode plate. Amplitude of sinusoidal alternating current is 5mV, test frequency was 500kHz-0.1Hz. The test device is shown in figure 2.

At the early stage of hydration (in 12h), the EIS of mortar samples was tested every half an hour. At the stable stage of hydration(1-28d), the EIS of mortar samples was tested at 1d, 3d, 7d, 11d, 14d
and 28d.

![Figure 2 Experimental setup for EIS](image)

3. Results and discussion

3.1 Electrochemical impedance spectroscopy of NMK cement mortar in early hydration stage

3.1.1 Electrochemical impedance spectroscopy of ordinary cement mortar in early hydration stage

The Nyquis diagram (in high frequency) of ordinary cement mortar (NMK0) in early hydration stage (1h, 4.5h, 10.5h and 12.0h) are shown in figure 3. For comparison, Nyquist diagram (in high frequency) of saturated Ca (OH)₂ solution under the same test conditions is also shown in figure 3.

![Figure 3 Nyquist plots of ordinary cement mortar in early hydration stage](image)

The results shows that when the age is 1h, there is a inductive arc with a tiny radius in the high frequency region of the EIS. Its morphology is closer to the high frequency curve of impedance spectrum of saturated Ca (OH)₂ solution under the same test conditions. There is no randles type curve in EIS of NMK0[9]. The above phenomenon shows that in early hydration stage (earlier than 12 hours), there is no electrochemical reaction in ordinary cement mortar, the pore structure of ordinary cement mortar has not been formed. The internal structur of ordinary cement mortar is filled with a large number of solutions with alkali metal ions. With the increase of hydration age, the inductive arc radius in the high frequency region of EIS tends to decrease (from 4.5H to 12h, the longitudinal coordinate of the top of inductive reactance arc decreases from 1.966 Ω to 0.826 Ω). Its shows that with the development of hydration, the inductive arc of cement mortar is disappearing and the pore structure begins to form.

3.1.2 Electrochemical impedance spectroscopy of NMK cement mortar in early hydration stage

The Nyquis diagram (in high frequency) of NMK cement mortar in early hydration stage (1h, 4.5h, 10.5h and 12.0h) are shown in figure 4. The results shows that the inductive arc of NMK cement mortar in high frequency region decreases with the increase of curing time. NMK obviously accelerates the reduction of inductive arc in high frequency region of cement mortar (as 12h an example, the ordinate of inductive arc vertex of NMK0, NMK3, NMK5 and NMK7 are 0.826 Ω, 0.805 Ω, 0.665 Ω and 0.400 Ω). The research shows that the process of cement mortar transformation from the early hydration stage to the stable hydration stage, the high frequency region of EIS will go through three stages successively: inductive arc, negative capacitance arc and positive capacitance arc.
It's shown that with the increase of curing age, the inductive arc in high frequency region of cement mortar decreases continuously. The above test results show that the EIS of cement mortar in high frequency region is changing from inductive arc to positive capacitance with the increase of curing time. The hydration process is changing from early hydration stage to stable hydration stage. NMK can obviously promote the transformation process and the higher the content of MK, the more obvious the promoting effect is.

The cross point between high frequency region of EIS and abscissa axis is pore solution resistance $R_0$. The pore solution resistance $R_0$ of NMK cement mortar within 12h hydration is shown in table 3. With the increase of hydration time, the pore solution resistance $R_0$ of NMK cement mortar increases. The higher NMK content is, the greater resistance $R_0$ of NMK cement mortar is. The $R_0$ value of NMK7 increased by 11.5% compared with NMK0 at curing 12h. The increase of $R_0$ with curing age is mainly due to the decrease of porosity caused by hydration products and nmk occupying the internal space of cement mortar and then block the ion current conduction in the pore solution.

Test results in figure 4 and table 3 show that NMK promotes the hydration of cement mortar in the early hydration stage. The higher NMK content is, the more significant the effect is.

![Nyquist plots of cement mortars with NMK in early stage of hydration](image)

The Nyquist plots show the impedance data of cement mortars with NMK in early stage of hydration.

**Figure 4 Nyquist plots of cement mortars with NMK in early stage of hydration**

| Time(h) | $R_0$ (Ω) |
|---------|------------|
| NMK0    | 43         |
| NMK3    | 46         |
| NMK5    | 49         |
| NMK7    | 50         |

**Table 3 $R_0$ of cement NMK mortars in 12h**

| Time(h) | NMK0 | NMK3 | NMK5 | NMK7 |
|---------|------|------|------|------|
| 1.0     | 43   | 46   | 49   | 50   |
| 4.5     | 44   | 47   | 49   | 51   |
| 10.5    | 72   | 79   | 81   | 82   |
| 12.0    | 87   | 94   | 95   | 97   |
3.2 Electrochemical impedance spectroscopy of NMK cement mortar in stable hydration stage

Figure 5 is Nyquist diagram of NMK cement mortar and common mortar at different curing ages. It shows that the topological structure of EIS of MK cement mortar at different ages is similar. They are composed of semicircles in the high frequency region and inclined straight lines in the low frequency region. Figure 5 also shows that: (1) for the same content of NMK cement mortar, with the increase of age, the EIS curve in Nyquist diagram shifts to the right as a whole, and the capacitive arc radius in high frequency region of the curve increases; (2) for the same curing age, with the increase of NMK content, the capacitive arc radius in high frequency region of the curve increases.

Figure 5 Nyquist plots of cement mortar with NMK in stabilization stage of hydration

The capacitive arc radius of EIS in high frequency region of cement-based materials is charge transfer resistance \( R_{ct} \). \( R_{ct} \) can reflect the degree of hydration of cement-based materials, and the larger \( R_{ct} \) is, the higher the hydration degree of cement-based materials is [10]. To obtain charge transfer resistance \( R_{ct} \) of NMK cement mortar, the equivalent circuit model in reference [7] is employed to calculate \( R_{ct} \) of EIS of NMK cement mortar. The \( R_{ct} \) values are listed in table 3. Table 3 shows that \( R_{ct} \) value of cement mortar increases with the increase of NMK content at same age. For curing 28 d, the \( R_{ct} \) value of NMK7 is 2 times of NMK0. The \( R_{ct} \) value of cement mortar with the same NMK content increases with the increase of curing age.

| Time(d) | \( R_{ct} \) (Ω) |
|---------|------------------|
| 1       | 40               | 92   | 102  | 150 |
| 3       | 255              | 300  | 360  | 388 |
| 7       | 518              | 702  | 718  | 766 |
| 11      | 1039             | 1317 | 1306 | 1477|
| 14      | 1143             | 1559 | 1801 | 2056|
| 28      | 1338             | 1671 | 2401 | 2611|

Table 4 \( R_{ct} \) values of cement mortars with NMK at various curing ages
Figure 6 is Bode diagram of EIS of NMK cement mortar at different ages. Bode diagram is another expression of EIS, which can reflect the variation of impedance mode $|Z|$ with frequency. Figure 6 shows that: (1) for the same content of NMK cement mortar, with the increase of age, the EIS curve in high frequency region of Bode diagram move upward; (2) for the same curing age, with the increase of NMK content, the EIS curve in high frequency region of Bode diagram move upward.

![Bode plots of cement mortar with NMK in stabilization stage of hydration](image)

Table 5 shows $|Z|$ value of high frequency region (take 100kHz as an example) of NMK cement mortar, which is calculated from Bode diagram of NMK cement mortar in figure 6. Table 5 shows that, the impedance mode $|Z|$ in high frequency region increases with the increase of NMK content at the same curing age. The $|Z|$ value of NMK7 increased about 1.6 times than that of NMK0 for curing 28 d. The $|Z|$ value of cement mortar with same NMK content increases with the increase of curing age.

The results in table 4-5 and figure 6-7 show that NMK promotes the hydration process of cement mortar during the stale hydration stage, and the higher NMK content, the more obvious the effect of promoting the hydration.

Table 5 $|Z|$ values of cement mortars with NMK at various curing ages (100kHz)

| Time (d) | NMK0 | NMK3 | NMK5 | NMK7 |
|---|---|---|---|---|
| 1 | 190 | 201 | 202 | 197 |
| 3 | 550 | 601 | 598 | 608 |
| 7 | 789 | 867 | 919 | 912 |
| 11 | 1160 | 1352 | 1363 | 1490 |
| 14 | 1455 | 1648 | 1850 | 1984 |
| 28 | 1665 | 2163 | 2377 | 2602 |

3.3 Effect of NMK on pore structure of cement mortar

EIS can not only reflect the hydration process of cement-based materials, but also reflect the pore
structure of cement-based materials[11]. A simplified microstructure model of cement-based materials is proposed in reference [11]. It is shown in figure 7. In this model, the conductive paths in cement-based materials are classified into three categories: continuous conduction path (CCP), discontinuous conductive paths (DCP), insulator conductive paths (ICP). The conduction of current in CCP channel is in pore solution; The current in DCP channel is alternately conducted by cement-based materials and pore solution (It is due to the blocking effect of disconnected points, as shown in figure 7); the conduction of current in the ICP channel is completely through the cement-based material.

![Figure 7. Simplified microstructure of cementitious materials](image1)

According to the equivalent circuit model proposed in reference [11], the change of resistance $R_{CCP}$ value of CCP channel is shown in figure 8. It shows that $R_{CCP}$ value of cement mortar increases with the increase of NMK at the same curing age. In addition to filling pores, NMK promotes the hydration of cement mortar due to small size effect, pozzolanic effect and dilution effect. NMK promoted the hydration of cement mortar, and more hydrated products (such as hydrated calcium silicate) was generated in NMK cement mortar at the same curing age. The hydration products fill the pores of NMK cement mortar, reduce the number of connecting channels in NMK cement mortar, improve the pore structure of the NMK cement mortar, and hinder the ion conduction in pore solution of NMK cement mortar. Other research shows that NMK can improve the chloride diffusion coefficient and reduce the porosity of cement-based materials[3], it confirms the results of this paper. The $R_{CCP}$ of cement mortars with NMK contents of 3%, 5% and 7% were 28.7%, 43.4% and 71.1% higher than that of ordinary mortar for curing 28 d.

![Figure 8. Resistance of Continuous conductive path](image2)

4. Conclusion
In this paper, the influence of NMK incorporation on the hydration of cement mortar was determined by EIS. The EIS of NMK cement mortar in the early hydration stage (1-12h) and the stable hydration stage (1-28d) was analyzed. The main conclusions can be drawn:

1. In the early hydration stage, NMK accelerated disappearance of inductive arc in high frequency region of EIS, improves the resistance of cement mortar pore solution, and promotes the hydration of cement mortar.

2. In the stable hydration stage, NMK increases capacitive arc radius in the high frequency region of EIS at same curing age, improving charge transfer resistance $R_{ct}$ and high frequency impedance mode $|Z|$, and promotes the hydration of cement mortar.

3. NMK can improve the pore structure of cement mortar, increase the resistance of continuous conduction path $R_{CCP}$, and block ion conduction in the pore solution of cement mortar. The $R_{CCP}$ of cement mortars with NMK contents of 3%, 5% and 7% were 28.7%, 43.4% and 71.1% higher than that of ordinary mortar for curing 28 d.
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