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Study of the Alkali activated Geopolymer by AC Impedance Spectroscopy

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Abstract: AC impedance spectroscopy was used to study the setting of alkali-activated geopolymers. Results show that electrochemical theory has certain advantages in analysis of the continuous microstructural changes of geopolymers in the process of geopolymerization. Setting process of alkali-activated geopolymer was divided into several stages according to the AC impedance spectra. AC impedance spectroscopy can be used to study the effect of the modulus and amount of activator on the microstructural change.

1. Introduction

Geopolymer is a kind of green and environmentally friendly materials and can be synthesised by mineral, solid waste and artificial silicon-aluminum activated by alkali or acid at normal temperature. Geopolymer is a three-dimensional network which is made up of Si-Al-O (-Si-O-Al-O-), Si-Al-Si-O (-Si-O-Al-O-Si-O-) and Si-Al disiloxane (-Si-O-Al-O-Si-O-Si-O-). Most research focused on the high-performance, high strength, high temperature resistance, corrosion resistance and durability of geopolymer¹, little reports about the setting process of geopolymer was found.

AC impedance spectroscopy has been widely used in some researches on hydration reaction of cement effectively, because of advantages of short testing time, non-destructive testing, stable measurement results and good regularity. In recent years, AC impedance spectroscopy was widely used to characterize the setting process and internal microstructure of cement²⁻⁵. Study the setting process of geopolymer by AC impedance spectroscopy should be very interesting. In this paper, electrochemical properties of alkali-activated geopolymers has been studied by AC impedance spectroscopy. The electrochemical activity and the setting time were evaluated by the EIS characteristics of geopolymer. The application of AC impedance technology to the detection of the electrochemical properties of geopolymers is not only beneficial to the nondestructive testing of materials, but also conducive to the development of geopolymer cementitious materials with excellent properties. It has academic value and practical significance for the development and application of geopolymers.

2. Experiment

2.1 Raw Materials

Coal gangue powder was calcined at 800°C for 4 hours to get metakaolin. Sodium silicate, sodium hydroxide and distilled water was used to prepare activation.



2.2 Sample Preparation

Water glass water solution was added to a certain amount of metakaolin, the mixture was mechanically stirred and then was poured into the 40 mm x 40 mm x 160 mm mold . After vibration, samples were put into a curing for curing, the curing temperature was 30 °C and a humidity more than 99%. Some mixture was poured into 40mm x 40mm x 160mm plastic mold, and two stainless steel electrodes are fixed on two relative parallel surfaces.

2.3 AC Impedance Measurement

CHI660E electrochemical workstation produced by American CH Instrument Ins Company was used in the experiment. The amplitude of sinusoidal voltage signal is 5 mV, and the measuring frequency range is from 1Hz to 100KHz. Five points are measured in each measuring level. Chi660E electrochemical testing software is used.

3. Results and Discussion

3.1 Impedance Spectroscopy at Various reaction Times

The theory of electrochemistry demonstrates that a perfect semicircle across a real axis occurs on an impedance complex plane when the concentration polarization is negligible in the equivalent circuit.

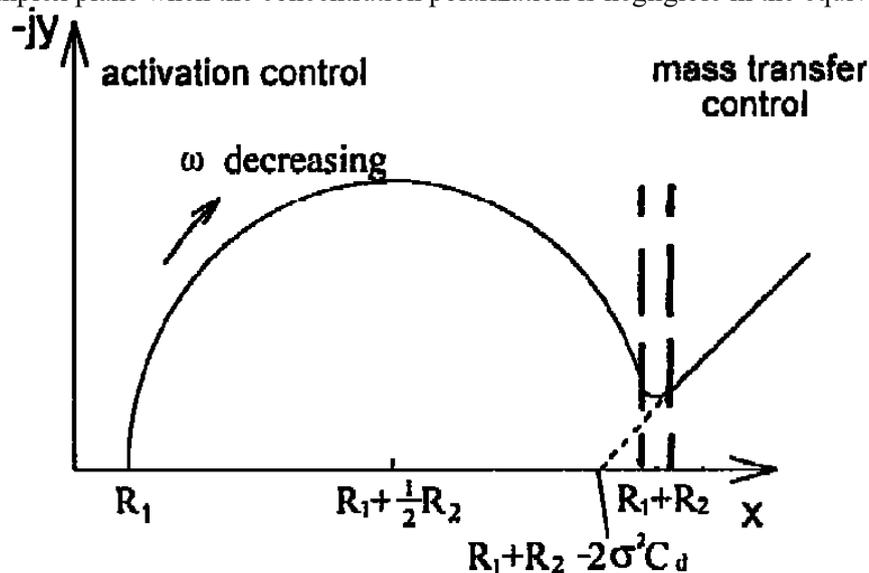


Figure 1. Impedance spectrum of equivalent circuit in the presence of concentration polarization.

An impedance spectrum in the presence of polarization is shown in Fig. 1, in which can be seen a semi-circle in a high-frequency arc (HFA) and an oblique line, i.e., Warburg impedance, describing the mass transfer process involving diffusion in a low-frequency arc (LFA). Extending the oblique line, the intersection with the real axis is at $R_1 + R_2 - 2\sigma_2 C_d$. R_1 is the high-frequency resistance, R_2 is the total electrical resistance whose absolute value is equivalent to the diam. R_1 is related to the measurement conditions, and R_2 is determined by the porosity and concentration of solution, and can be expressed as

$$R_2 = \frac{k_1}{pr} \left(1 + \frac{k_2}{\sqrt{C}} \right) \quad (1)$$

where P is the porosity, r is the mean size of the pore, and C is the concentration of ions.

For the portland cement system, the value of $2\sigma_2 C_d$ is small and the oblique line intersects the real axis. R_1 is related to the measurement conditions and R_2 is determined by P and r . P is the porosity while r is average pore size, C_d is the concentration of ions⁶.

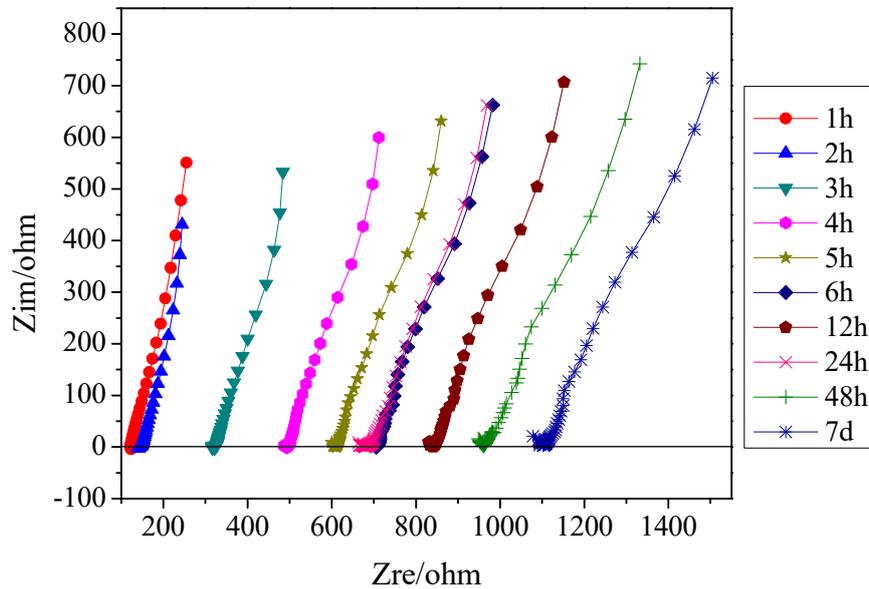
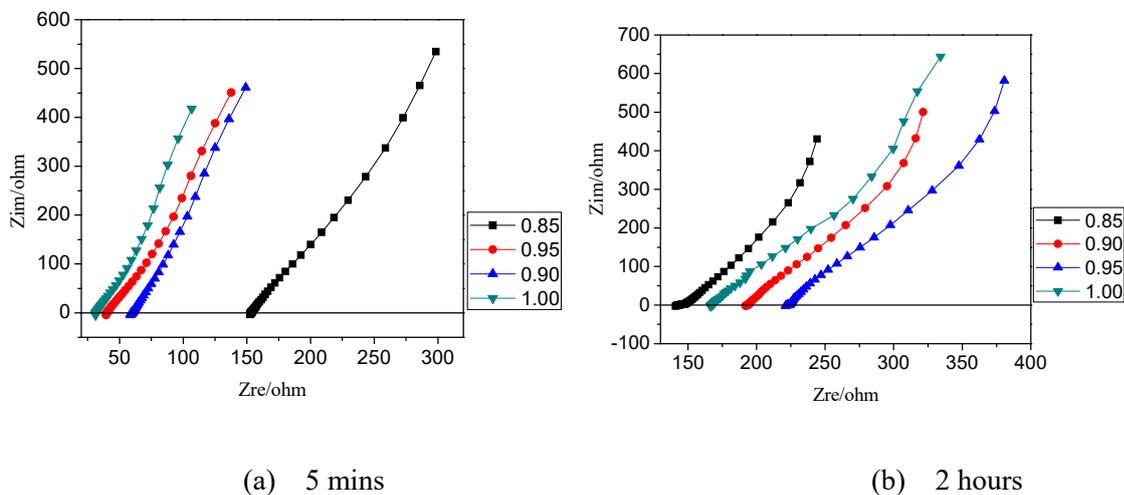


Figure 2 . Impedance spectra of polymerization reactions at different times

The AC impedance behavior of geopolymerization at different times is illustrated in figure 2. W/S is the ratio of water to powder. As shown in figure 2, no semicircle was observed between the ranges of 1Hz to 100 kHz. R_1 is a constant in the process of geopolymerization, the changes of porosity and pore size⁷ depend on R_2 , The microstructural changes can be investigated qualitatively according to the intercepts and their variation although the absolute values cannot be calculated. And the change rule of microstructures can be determined qualitatively by the relative position and its change of intersecting line and real axis.

It is obvious that the lines of impedance spectra in the whole process are parallel to each other in figure 2. The value of the intercept increases evenly within the first 24h then decreases. The increase of R_2 indicates a decrease of $P \cdot r$ ⁸. It can be inferred that $P \cdot r$ almost decreases linearly within 24h, and then increases after 24h.

3.2 Impedance Spectroscopy of different liquid-solid ratios



(a) 5 mins

(b) 2 hours

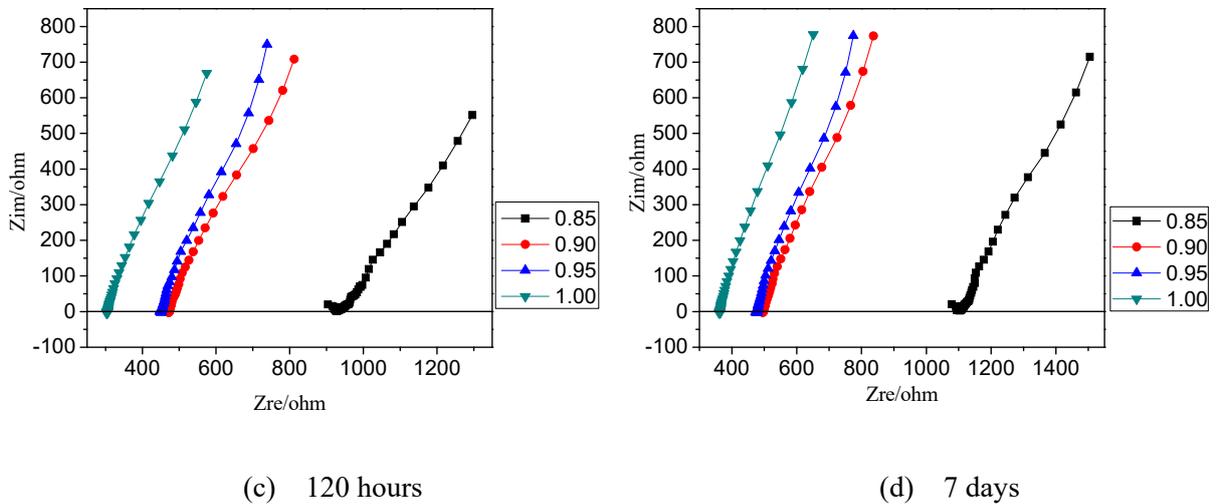
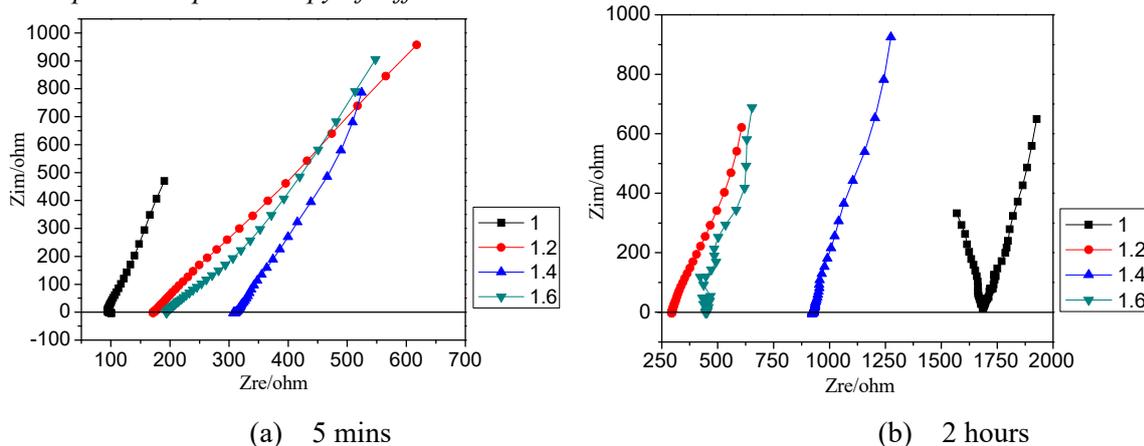


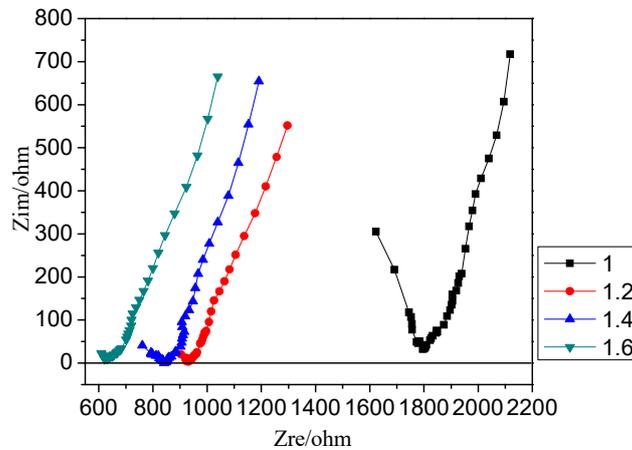
Figure 3. Impedance Spectroscopy at Various liquid-solid ratios

The AC impedance spectra of different liquid-solid ratios are shown in figure 3. At the initial stage, the curves are close to each other. The intercept values of samples with different liquid-solid ratios are in the order of 1.00, 0.95, 0.90 and 0.85. At this stage, the current of geopolymer slurry is mainly related to the applied voltage E and the parameter θ related to the surface state of metakaolin particles⁹. θ is the ratio of the dissolved surface area to the total surface area of metakaolin particles. Therefore, the increasing θ will result in the increase of the plasma current.

The impedance real part data of W/S0.85 is obviously lower than that of other mixtures after 2 h. With the dissolution of Si and Al, the ion concentration in the geopolymer slurry increases, the resistance value of the sample decreases gradually, and the intercept of W/S=0.85 samples changes most. After 120 h, the intercept changed obviously. The intercept of W/S=0.85 samples reach the maximum value, and porosity and average pore size reaches the minimum according to Eq. (1). It indicates that W/S=0.85 is the best liquid - solid ratio.

3.3 Impedance Spectroscopy of different activator modules



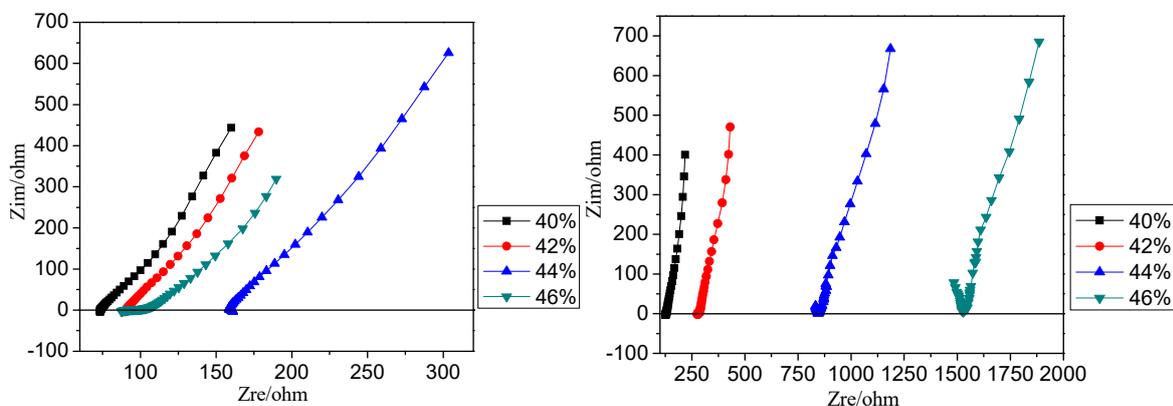


(c) 120 hours

Figure 4. Impedance Spectroscopy at Various activator modules

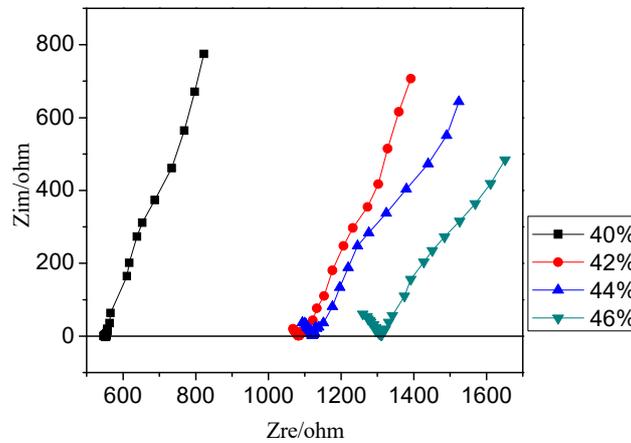
In the process of depolymerisation, there was no obvious electrochemical reaction in the pore solution of the slurry. After epolymerisation geopolymer gel generated in large quantities, and AC impedance changed to Quasi Randles type gradually. The Nyquist diagram of the hardened geopolymer at stable stage shows quasi-Randles type. The angle between the oblique line and the real axis deviates by 45 degrees due to the flat half circle or center deviation caused by the normal phase angle element⁶. Figure 4 (a) and (b) show that the intercept order of different activator modules according to 1,1.2,1.6 and 1.4 at the beginning 5 minutes. The intercept of sample with modulus 1 is smaller than that of other samples. After 2 h, the quasi-Randles characteristic appeared for activator modulus 1 samples. It indicates modulus 1 samples have the most compact construction. In figure 4 (c), after 120 h, the Nyquist diagrams of 4 different activator modulus samples according to 1.2, 1.4 and 1.6 display the quasi-Randles characteristics, and there are slight bumps in the high frequency region, but it is not obvious and the diameters are small. For R_2 , relative to 120 h, the density of slurry increases, and the parameters will change. Changes are caused by changes of microstructure of geopolymer slurry. AC impedance spectroscopy is correspond the changes closely. The intercept of the sample with activator modulus 1.2 changed the most. After 120 h, the intercept of modulus 1 samples did not change significantly. The results show that the modulus 1 samples are more compact after 120 h. This is in agreement with the test results of compressive strength¹⁰.

3.4 Impedance Spectroscopy of different activator dosage



(a) 5 mins

(b) 2 hours



(c) 48 hours

Figure 5. Impedance Spectroscopy at Various activator dosage

Figure 5 shows the AC impedance spectra of different activator dosages (the percentage is the weight ratio between activator and metakaolin). Figure 5 (a) and (b) show that the intercept of the sample with 46% of the activator dosage changes most obviously, followed by the sample with 44% of the activator dosage. The results showed that 2 h, 46% of the samples were densest and the gel content of polymer was the highest. In figure 5 (c), the intercept of 46% sample decreased after 48 h. The shape of Nyquist curve will not change after the geopolymerization has entered a stable period, and the quasi-Randles type is maintained.

3.5 Time Characteristic Curve of Real Part at 1kHz

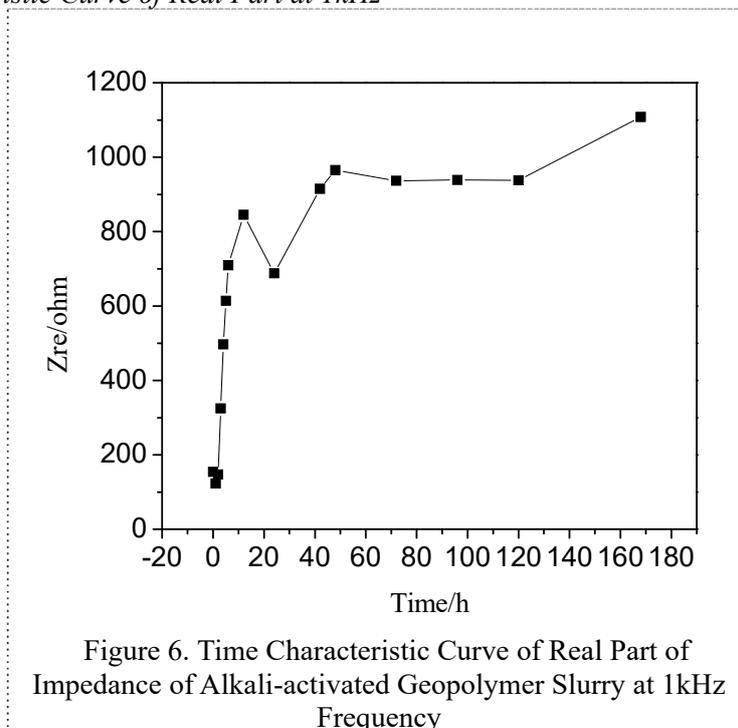


Figure 6. Time Characteristic Curve of Real Part of Impedance of Alkali-activated Geopolymer Slurry at 1kHz Frequency

The variation of real and imaginary impedance parts in 4320 minutes is defined as the following three characteristic points: minimum value, first peak value and first valley value. Based on the

characteristic points, the condensation reaction process of alkali-activated geopolymer slurry during initial period can be divided into dissolution period, polymerization period, solidification period and hardening period.

Dissolution period: In figure 6, the real part of impedance gradually decreases within the first 1 h. This is due to the dissolution of Si and Al under the action of OH-ion¹¹. In this condition, the ion concentration in liquid phase increases rapidly, while the pore structure has not yet formed, and the geological polymer products are less, which makes the resistivity of liquid phase decrease obviously.

Polymerization period: Slow increase of intercept means that the conductivity of samples decreases, which indicates that the increase of geopolymer leads to the decrease of porosity of samples. This is because the silicate and aluminate ions dissolved during depropagation, then polymer monomers are connected to geopolymer. This means that alkali-activated geopolymer slurry begins to coagulate and gradually loses plasticity. At the same time, the formation of products of geopolymerization consumes ions of ions in solution. Silicon monomers in water glass adsorb on the surface of metakaolin particles, shield the surface charge of metakaolin particles and reduce the double-layer force between particles. The continuous formation of geopolymer results in the decrease of porosity, blocks the conductive space of ions and weakens the conductivity of samples. As shown in figure 3 (a), the time difference between the first peak and the minimum value is small, because the distance between metakaolin particles in alkali-activated geopolymer slurry is relatively close, and the conductive space of ions can be blocked by fewer reaction products.

Solidification period: The decrease of intercept means that the conductivity of the sample became higher. It can be explained that as the product of geopolymerization encapsulates the surface of incompletely reacted metakaolin particles, an encapsulation layer was formed. With the accumulation of the reaction product, its osmotic pressure increases, and results in the rupture of the encapsulation layer. Meanwhile the ionic dissolution and precipitation rate increase, the ionic conductivity space is connected, which leads to the slow enhancement of the conductivity of the samples.

Harden period: With the continuous generation of reaction products, the fluidity of slurry become low. Incomplete reacted metakaolin particle surface coating is increasing, further blocking ionic conduction space, resulting in an increase of intercept. During harden period, the resistive component of impedance spectra of alkali-activated geopolymer slurry has a larger growth slope. Because the liquid resistivity of the same sample changes little at the later stage of reaction. According to Archie's law, the increase of matrix impedance means the decrease of liquid space with conductive properties. The increase of hydration products per unit time and volume is larger in unit volume, which means there is a larger change in porosity and a larger growth slope of the real part curve of impedance spectrum.

4. Conclusion

(1) When the liquid-solid ratio is 0.85, the ion concentration of the geopolymer slurry during the dissolution period is the highest, which is most conducive to the geopolymerization reaction.

(2) The sample with activator modulus of 1.2 has the largest intercept. The product of porosity and average pore size is the smallest, indicating that the geopolymer has the most compact structure.

(3) The sample with 46% activator had the largest intercept after 48 hours, and has a downward trend. And the intercept of the sample of other admixture is increasing ceaselessly. This indicates that in the later stage of reaction, excessive dosage will have a negative effect on the porosity of samples.

(4) In the geopolymer process, the resistive component curve of complex impedance decreases then became increases. After that complex impedance decreases again and then tend to be increases.

(5) During hardening period, the resistive component curve of impedance spectra of alkali-activated geopolymer slurry has a larger growth slope.

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