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In situ monitoring of the hydration process of K-PS geopolymer cement with ESEM

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Abstract

Environmental scanning electron microscope (ESEM) was used to in situ quantitatively study the hydration process of K-PS geopolymer cement under an 80% RH environment. An energy dispersion X-ray analysis (EDXA) was also employed to distinguish the chemical composition of hydration product. The ESEM micrographs showed that metakaolin particles pack loosely at 10 min after mixing, resulting in the existence of many large voids. As hydration proceeds, a lot of gels were seen and gradually precipitated on the surfaces of these particles. At later stage, these particles were wrapped by thick gel layers and their interspaces were almost completely filled. The corresponding EDXA results illustrated that the molar ratios of K/Al increase while Si/Al decrease with the development of hydration. As a result, the molar ratios of K/Al and Si/Al of hydration products at an age of 4 h amounted to 0.99 and 1.49, respectively, which were close to the theoretical values (K/Al = 1.0, Si/Al = 1.0 for K-PS geopolymer cement paste). In addition, well-developed crystals could not been found at any ages; instead, spongelike amorphous gels were always been observed.

Keywords: K-PS geopolymer cement; Hydration process; ESEM; In situ quantitatively study

1. Introduction

Geopolymers are amorphous three-dimensional aluminosilicate binder materials, which were firstly discovered by Prof. Glukhovsky in the former Soviet Union in the 1950s. Davidovits [1] in France also started the similar work in the later 1970s and called it Geopolymer. Geopolymer binder materials can be synthesized by mixing aluminosilicate reactive materials (such as metakaolin) and strong alkaline solutions (such as NaOH or KOH), then curing at room temperature. Under a strong alkaline solution, aluminosilicate reactive materials are rapidly dissolved into solution to form free SiO_4 and AlO_4 tetrahedral units. With the development of reaction, water is gradually split out and these SiO_4 and AlO_4 tetrahedral clusters are linked alternatively to yield polymeric precursors ($-SiO_4-AlO_4-$, $-SiO_4-AlO_4-SiO_4-$, or $-SiO_4-AlO_4-SiO_4-SiO_4-$) by sharing all oxygen atoms between two tetrahedral units and thereby forming amorphous geopolymers [2]. According to the structure, geopolymer can be expressed by the following empirical formula [3]:

$$R_n\{-(SiO_2)_z - AlO_2-\}_n \times wH_2O$$

Where, R is a cation such as potassium and sodium; n is the degree of polycondensation; z is 1, 2, and 3; and w is binding water amount. The most common types of geopolymers are as follows:

Types of species	Abbreviations
1. Poly(sialate)	
$R_n-(-Si-O-Al-O-)_n-$	R-PS
2. Poly(sialate-siloxo-)	
$R_n-(-Si-O-Al-O-Si-O-)_n-$	R-PSS
3. Poly(sialate-disiloxo-)	
$R_n-(-Si-O-Al-O-Si-O-Si-O-)_n-$	R-PSDS

Compared to Portland cement, Geopolymers possess the following characteristics [4–7]:

The production of geopolymer cement requires relative low temperature (600–800 °C) and emits less CO_2. Reasonable strength can be obtained in a short period at room temperature. In most cases, 70% of the final compressive

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strength is developed in the first 4 h of setting. Low permeability, comparable to natural granite, is another property of geopolymers. It is also reported that resistance to fire and acid attacks for geopolymers are substantially superior to those for Portland cement. Apart from their high early strength, low permeability, and good fire and acid resistance, geopolymers also attain higher unconfined compressive strength and shrink much less than Portland cement. Other documented properties include good resistance to freeze–thaw cycles, as well as excellent solidification of heavy metal ions contained within the geopolymer structure.

These properties make geopolymer cement a strong candidate for substituting Portland cement applied in the fields of civil, bridge, pavement, hydraulic, underground, and military engineering [8].

Geopolymer cement is a new generation of inorganic Si–Al binder materials, which is quite different from Portland cement in the aspects of the microstructures, chemical composition, and hydration process. What are the morphologies and chemical compositions of hydration products for geopolymer cement paste? How do these products develop with time? The answers to these above questions significantly affect the further development and application of geopolymer cement in field construction engineering.

Conventionally, scanning electron microscope (SEM) has been widely employed to characterize the morphology and microstructure of hydration products. Before performing SEM, samples must be dried and coated with thin layer of gold or carbon to prevent the surface from charging while being observed. These pretreatment on the surface of sample bring about three disadvantages: First, samples must have enough strength to withstand drying and coating treatment, which make it difficult to obverse the hydration process at the early stage. Second, drying and vacuuming may cause a distortion of the fragile microstructure. Third, the continuous in situ changes in chemical compositions and morphology cannot be realized by using SEM. Fortunately, an advanced microscopy technique—environmental scanning electron microscope (ESEM)—has been developed recently with the capability of observing continuous reacting process in "environment" atmosphere. Because of the application of multivacuum systems and gas second electron detector technique, ESEM have the following characteristics as compared to SEM [9–15]:

1. Sample preparation is very simple and convenient. Drying and coating treatments are not essential. Freshly mixing sample or harden paste can be directly placed into sample holder.
2. The "true" micrograph can be obtained using ESEM due to elimination of high vacuum.
3. The temperatures and relative humidity can be controlled by researchers to simulate a required environment, and multilocations on the surface of sample can be remembered in computer connected with ESEM apparatus.

These functions make it possible to follow the micrograph changes of hydration products of the same lactation with time at the early age of hydration process under moist condition. In addition, by means of energy dispersion X-ray analysis (EDXA) as supplementary equipment, ESEM can quantitatively identify the changes in chemical compositions on the surface of samples, which provide a further scientific insight into the reaction mechanism.

In this study, the changes in the micrographs and chemical compositions of the same location with time were monitored and recorded for K-PS geopolymer bulk paste by using ESEM and EDXA. The monitored period started from 10 min after the mixing of metakaolin and alkali accelerator and ended at an age of 4 h when 80% of the final strength can be achieved.

2. Materials and methods

2.1. Materials

Metakaolin used in this study was obtained by calcining kaolin at 700 °C for 12 h. It was used for reactive Si–Al cementitious materials.

Analytical grade KOH and potassium silicate solution with the molar ratio of SiO_2 to Na_2O of 3.3 were used as reagents.

Distilled water was used throughout.

2.2. Methods

2.2.1. Mixture proportion and sample preparation

In this study, KOH, potassium solution, and water were firstly mixed in a beaker and cooled up to room temperature, then powder metakaolin was added into the cooled alkaline solution and mixed for another 3 min. After that, the fresh geopolymer paste was rapidly poured into steel sample holder. The prepared sample was instantly placed into the sample chamber in ESEM and observation started. The morphologies and corresponding EDXA were measured and recorded at an age of 10 min, 3 h, 6 h, and 9 h under an 80% RH condition. The sample chamber in ESEM was kept in carbon-oxide-free environment. These operations described above required to be completed in 5 to 10 min. The purpose of this study was to document the microstructure characteristics and their evolution with time for K-PS geopolymer cement paste during the hydration process. The details of mixture proportion and compressive strength of K-PS geopolymer cement paste were given in Table 1.

2.2.2. Instrument and test parameters

In this study, XL30-ESEM together with EDXA was used to characterize the early age microstructure and chemical composition changes of hydration products with time at one fixed location. The following test parameters were

Table 1
Mixture proportions and compressive strength of K-PS geopolymer

Oxidants ratio of K-PS geopolymer cement (molar/molar)			Compressive strength (MPa)				
SiO_2/Al_2O_3	K_2O/Al_2O_3	H_2O/K_2O	1.5 h	4 h	24 h	3 days	28 days
2.5	0.8	5.64	8.7	9.9	10.8	11.5	12.2

employed in this study: accelerating voltage of 20 keV, pressure in sample chamber of 4.2 Torr, 80% RH, and three orders of magnification of × 3200, × 6400, and × 10,000. In order to in situ follow morphology changes with time, the sample was kept in sample chamber until the end of observation. Because observed locations were automatically remembered and locked in computer memory, these ESEM micrographs at different time theoretically correspond to the same location.

Considering the very rapid hydration reaction for K-PS geopolymer, 80% or higher of compressive strength can be achieved by an age of 4 h. After that, the strength development is very slow. Thus, ESEM observation started from 10 min after mixing and ended at 4 h in this investigation.

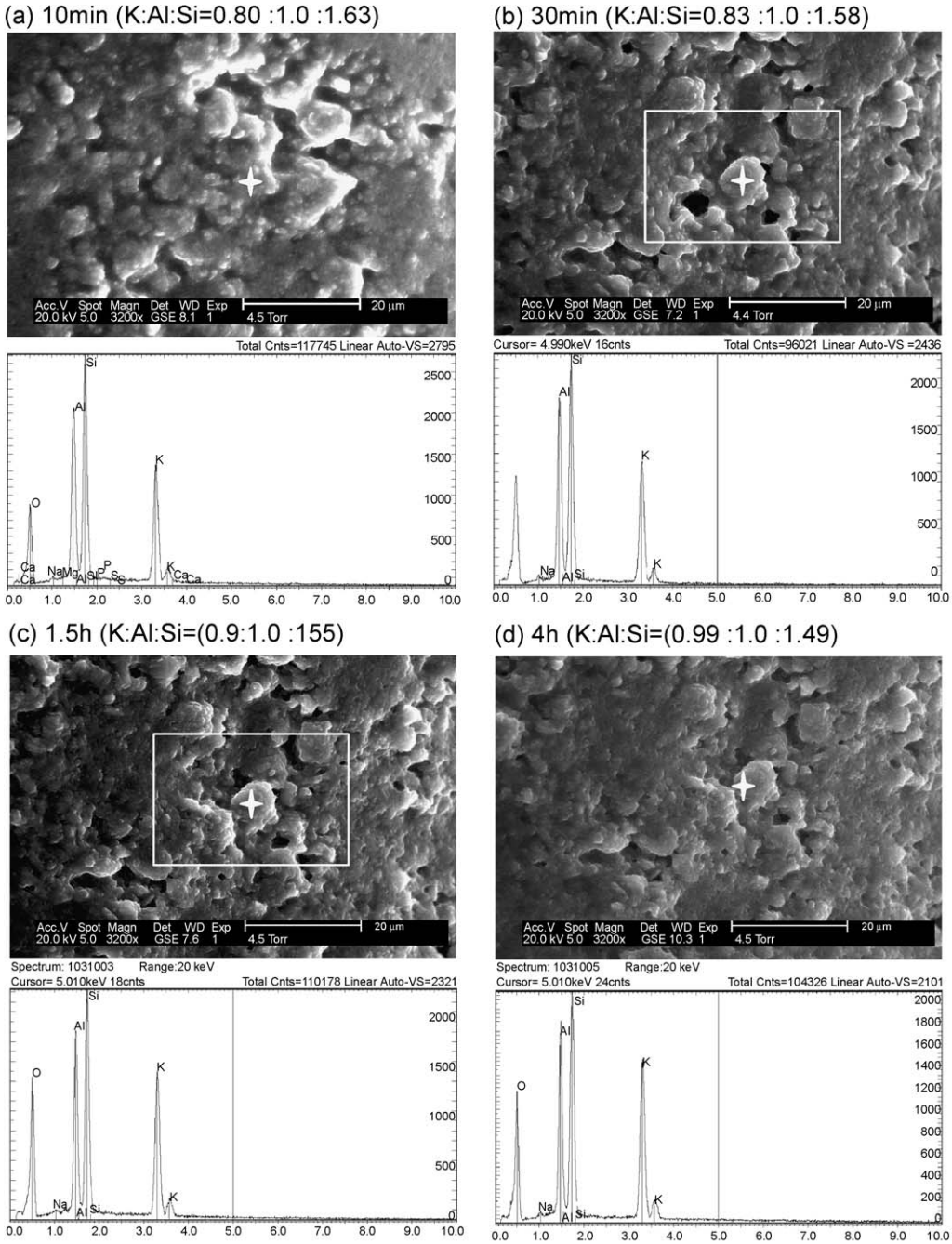

Fig. 1. In situ ESEM micrographs and EDXA of K-PS after different time of hydration (× 3200).

3. Results and analysis

3.1. In situ evolution of micrographs

Fig. 1 shows the changes in morphologies and chemical compositions of the fixed location in K-PS geopolymer paste from 10 min to 4 h after mixing. In order to observe the details more clearly, higher orders of magnitude of micrographs are also given in Figs. 2 and 3, respectively. The corresponding molar ratios of different elements are also listed. The observed location is marked by "cross" shape.

As can be found from Fig. 1a, the sphere-shaped metakaolin particles can be seen clearly at the beginning of hydration. These particles packed loosely and some void could be found. After 30 min, some spongelike amorphous gels started to appear and gradually precipitated and covered on the surface of metakaolin particles, resulting in the disappearance of sphere-shaped profiles (Fig. 1b). Moreover, some gels also filled the voids among the metakaolin particles, and the microstructure of K-PS geopolymer cement paste became relatively compacted. However, there were still few voids in geopolymer bulk paste due to the short hydration time. For example, two voids within the white square frame were observed in Fig. 1b. The details can clearly be distinguished by higher magnification of images as shown in Figs. 2a and 3a. If measuring the diameters of the two voids in Fig. 1b using the scale bar, it was shown that they were 5 and 2 μm, respectively. After 1.5 h, more gels produced inside these voids and extended outsides. As a result, the 5-μm diameter void was engulfed by a large amount of gels and 2-μm diameter void also reduced to 1.25 μm (Figs. 1c, 2b, and 3b). After 4 h, amorphous gels continuously formed and filled these smaller voids. The 1.25-μm diameter void in Fig. 1c further decreased to 1.15 μm (Fig. 1d). After 4 h, little difference in microstructures could be distinguished at different age, indicating the almost completion of hydration process. It should be note that no crystal with regular shape was found during the whole process of hydration.

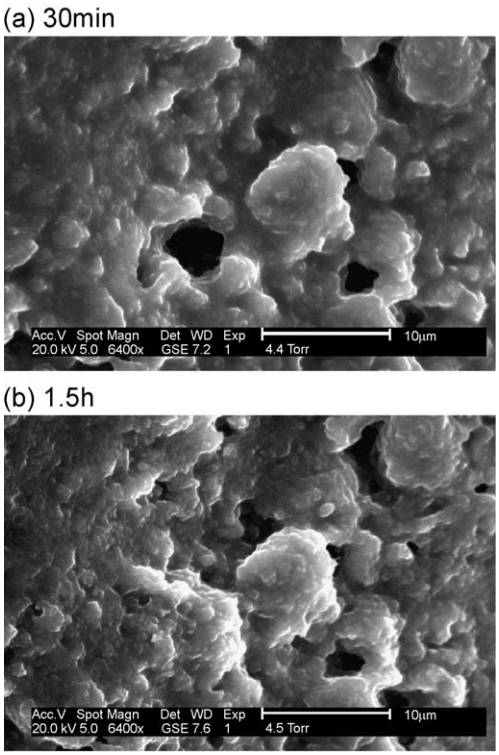

Fig. 2. ESEM micrographs of K-PS at the same location after different time of hydration (× 6400).

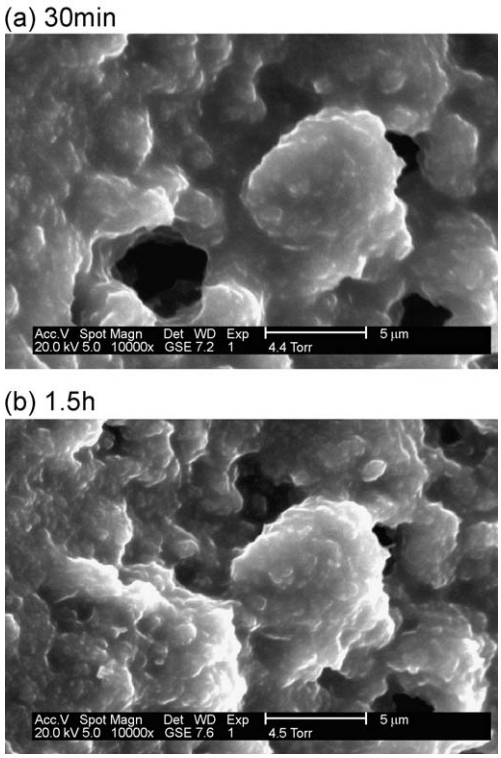

Fig. 3. ESEM micrographs of K-PS at the same location after different time of hydration (× 10,000).

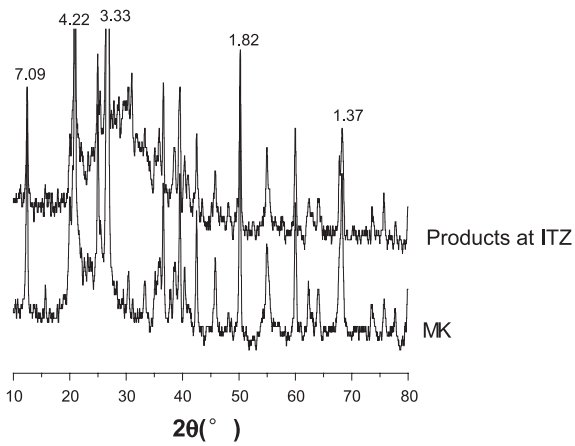

Fig. 4. XRD spectra of metakaolin and hydration products of K-PS geopolymer cement paste.

Based on these above ESEM micrographs, hydration products formed in K-PS geopolymer cement paste appear to be spongelike amorphous gels rather than well-developed regular crystals. However, XRD still need to be performed to confirm the "true" nature of these spongelike products. In this study, a little sample of powder products was scraped off from the surface of harden paste to conduct XRD test. In addition, XRD of metakaolin was also carried out to serve as a reference sample (Fig. 4). It was seen from Fig. 4 that a large diffuse halo peak at about 20°–40°($2\theta_{max}$ $CuK_{\acute{a}}$) showed in X-ray diffractogram of gel products. This means that gel products are mainly X-ray amorphous materials. In addition, several sharp characteristic peaks (7.09, 4.23, 3.33, 1.81, 1.54, and 1.37 Å) were also seen from Fig. 4. According to the XRD pattern, these peaks were qualified as kaolin and quartz. With respect of X-ray diffractogram of metakaolin, kaolin and quartzes are induced by metakaolin; and in the process of geo polysization, the kaolin and quartzes do not take part in reaction.

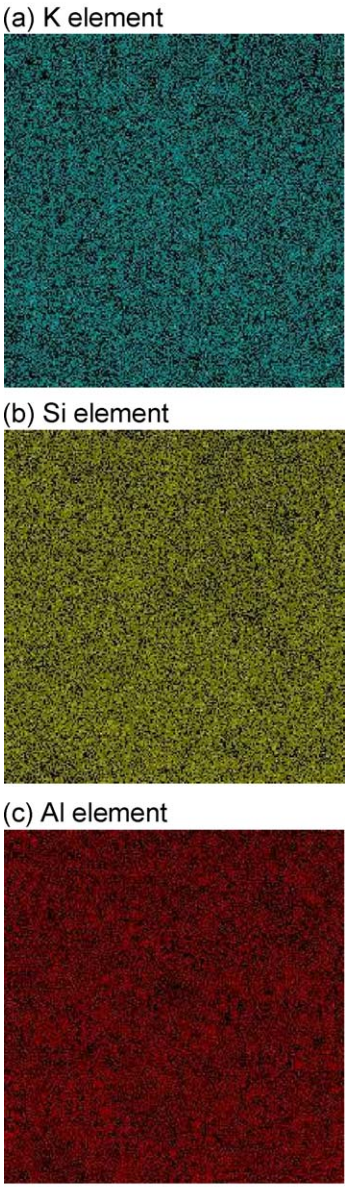

Fig. 5. Mapping of three types of elements (K, Si, and Al) of K-PS Geopolymer after 4 h hydration.

3.2. In situ evolution of chemical compositions

Fig. 1 also shows the evolution of EDXA spectra and molar ratios of different elements of the same location at different time. It was found that the molar ratio of K/Al increased while Si/Al showed a diminishing tendency with the development of hydration. For instance, at 10 min, the molar ratios of K/Al and Si/Al were 0.80 and 1.63, respectively. However, the corresponding values were 0.99 and 1.49 after 4 h, which showed a close tendency to the theoretical values of K-PS harden geopolymer paste (K/Al = 1.0, Si/Al = 1.0).

In addition, X-ray mappings of three elements (K, Si, and Al) of K-PS geopolymer cement paste at 4 h are also collected and recorded in Fig. 5. It can be seen from Fig. 5 that K, Si, and Al were uniformly distributed across the bulk paste. This means that the gel products are generated evenly during the whole process of hydration.

4. Conclusion

Based on the above ESEM and EDXA observations, the following conclusions can be drawn:

1. At early stage, the metakaolin particles pack loosely together resulting in the existence of many large voids. As hydration proceeds, gel products gradually precipitate on the surface of these particles and extend outsides; as a result, these voids were fully filled. At later stage, the metakaolin particles were wrapped by a thick gel layer, and the microstructure of geopolymer paste become very denser.
2. The molar ratios of K/Al increase while Si/Al decrease with the development of hydration. At an age of 4 h, the molar ratios of K/Al and Si/Al of hydration products amounted to 0.99 and 1.49, respectively, which were close to the theoretical values (K/Al = 1.0, Si/Al = 1.0).
3. Well-developed crystals could not been found in K-PS geopolymer cement bulk paste at any ages, while spongelike amorphous gel is always been observed.

Acknowledgements

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References

[1] J. Davidovits, Geopolymers and geopolymeric new materials, J. Therm. Anal. 35 (2) (1989) 429–441.

[2] J. Davidovits, M. Davidovits, Geopolymer: ultrahigh-temperature tooling material for the manufacture of advanced composites, in: R. Adsit, F. Gordaninejad (Eds.), 36th Annual SAMPE Symposium and Exhibition, Covina, CA, USA, vol. 36, pt 2, 1991, pp. 1939–1949.

[3] J. Davidovits, Geopolymer cement to minimize carbon-dioxde greenhouse-warming, in: M. Moukwa, SL. Sarkar, K. Luke, M.W. Grutzeck (Eds.), Cement-Based Materials: Present, Future, and Environmental Aspects, American Ceramic Society, Ceramic Transactions, Westerville, America, vol. 37, 1993, pp. 165–182.

[4] J. Davidovits, Properties of geopolymer cement, in: F. Škvára (Ed.), Proceedings 1st International Conference on Alkaline Cements and Concretes, Scientific Research Institute on Binders and Materials, Kiev State Technical University, Kiev Ukraine, 1994, pp. 131–149.

[5] R.E. Lyon, A. Foden, P.N. Balaguru, M. Davidovits, J. Davidovits, Fire-resistant aluminosilicate composites, J. Fire Mater. 21 (2) (1997) 67–73.

[6] J. Davidovits, High alkali cements for 21st century concretes, concrete technology, past, present, and future, in: P.K. Mehta (Ed.), American Concrete Institute, Detroit, SP-144 1994, pp. 383–397.

[7] J. Davidovits, Geopolymer chemistry and properties, J. Davidovits, J. Orlinsl (Eds.), Proceedings of the First European Conference on Soft Mineralogy 1, Geopolymer Institute, Compiegne, France, 1988, pp. 25–48.

[8] M. Mouret, A. Bascoul, G. Escadeillas, Microstructural features of concrete in relation to initial temperature—SEM and ESEM characterization, Cem. Concr. Res. 29 (3) (1999) 369–375.

[9] K.O. Kjellsen, H.M. Jenningst, Observations of microcracking in cement paste upon drying and rewetting by environmental scanning electron microscopy, Adv. Cem. Based Mater. 3 (1) (1996) 14–19.

[10] Z. Su, K. Sujata, et al, The evolution of the microstructure in styrene acrylate polymer-modified cement pastes at the early stage of cement hydration, Adv. Cem. Based Mater. 3 (3) (1996) 87–93.

[11] D. Zampini, S.P. Shah, Early age microstructure of the paste-aggregate interface and its evolution, J. Mater. Res. 13 (7) (1998) 1888–1898.

[12] S. Manjun, In-situ study of oxidation on iron surface with ESEM, Acta Metall. Sin. 36 (3) (2000) 230–240.

[13] Y. Limin, About environment scanning electron microscope, Modern Science Instrument 2 (2001) 53–56.

[14] Z. Wu, G. Shuyi, W. Xianlu, Key techniques of ESEM, Vacuum 4 (2001) 34–37.

[15] C. Changqi, Z. Wu, G. Shuyi, Vacuum system and imaging signal in environmental scanning electron microscope, Vac. Cryog. 7 (2) (2001) 122–124.