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Materials Letters 61 (2007) 1552–1557
materials letters
www.elsevier.com/locate/matlet

In situ observing the hydration process of K-PSS geopolymeric cement with environment scanning electron microscopy

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Received 16 February 2006; accepted 21 July 2006
Available online 17 August 2006

Abstract

The hydration process of K-PSS geopolymeric cement was in situ quantitatively investigated by environment scanning electron microscope (ESEM) under 80% relative humidity. An energy dispersion X-ray analysis (EDXA) was also employed to determine the chemical composition of the hydration product. The ESEM micrographs showed that metakaolin particles pack loosely at 10 min after an initial mixing, resulting in an existence of many large voids. As the hydration proceeded, some gels were produced and gradually precipitated on the surfaces of these particles. At a later stage, these particles were covered by thick gel layers, and their interspaces among the metakaolin particles were also completely filled up. The corresponding EDXA results illustrated that the molar ratios of K/Al and Si/Al decreased with the development of hydration. The molar ratios of K/Al and Si/Al of the hydration products at an age of 13 h amounted to 1.06 and 2.14 respectively, which were very close to the theoretical values (K/Al = 1.0, Si/Al = 2.0) for K-PSS geopolymeric cement hardened paste. In addition, well-developed crystals could not be found at any ages, instead sponge-like amorphous gels have always been observed during the whole hydration process.

Keywords: K-PSS geopolymeric cement; Hydration process; ESEM; In situ; Microstructure

1. Introduction

“Geopolymer” is a novel type of alumino-silicate cementitious material without CaO content, which was first introduced to the inorganic cementitious world by J. Davidovits at the end of the 1970s [1]. Subsequently, through his studies on geopolymer he proposed a hypothesis that ancient Egypt pyramids may be constructed by geopolymerization technology, rather than by rocks traditionally. This viewpoint at once receives a great deal of attention across the world. From then on, many researchers start to study geopolymer and its synthesizing technology, thus a new field of research and technology is rapidly developed in the recent 20 years.

Geopolymeric cement can be synthesized by mixing reactive alumino-silicate materials with less or no CaO content (such as metakaolin, dehydrated clay, Class F fly ash) and strong alkaline solutions (such as NaOH or KOH), then curing at room temperature. Under a strong alkaline solution, reactive alumino-silicate materials are rapidly dissolved into a solution to form free SiO_4 and AlO_4 tetrahedral units. With the development of the reaction, water is gradually split out and these SiO_4 and AlO_4 tetrahedral clusters are linked alternatively to yield polymeric precursors ($–SiO_4–AlO_4–$, or $–SiO_4–AlO_4–SiO_4–$, or $–SiO_4–AlO_4–SiO_4–SiO_4–$) by sharing all oxygen atoms between two tetrahedral units, and thereby forming amorphous geopolymeric products [2]. According to the structure, the geopolymer can be expressed in the following empirical formula [3]:

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

Where, R is cation such as potassium or sodium; n is the degree of polycondensation; z is 1, 2 and 3; w is the binding water amount. The most common types of geopolymer are listed in Table 1.

Geopolymer made with a reasonable mix-design and formulation exhibits superior properties compared to Portland concrete [4–7].

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0167-577X/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.matlet.2006.07.077

Table 1
The most common types of geopolymers

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

The production of geopolymers doesn't require high temperature as Portland cement. Geopolymeric cement can be formed at ambient temperature. In addition, CO_2 emission from the production process is 80%–90% less than Portland cement. Reasonable strength can be gained in a short period at room temperature. In most cases, 70% of the final compressive strength is developed in the first 4 h. Low permeability, comparable to natural granite, is another property of geopolymers. It is also reported that resistance to fire and acid attacks for geopolymers is substantially superior to that of Portland cement. Apart from their high early strength, low permeability and good fire and acid resistance, geopolymers also attain higher unconfined compressive strength and lower shrinkage than Portland cement. Other documented properties include good resistance to freeze–thaw cycles as well as excellent solidification of heavy metal ions.

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

Geopolymeric cement is quite different from Portland cement in the aspects of microstructures, chemical composition and hydration process. What are the morphologies and chemical compositions of hydration products for geopolymeric cement paste? How do these products develop with time? The answers to these above questions significantly affect the further development and application of geopolymeric cement in the field of construction.

Scanning electron microscope (SEM) has been widely used to characterize the morphology and microstructure of Portland cement hydration products. However, before performing SEM samples must be dried and coated with a thin layer of gold or carbon to prevent the surface from being charged whilst observing. These pre-treatment on sample will bring about 3 disadvantages: first, the samples must have enough strength to withstand drying and coating treatment, which make it difficult to observe hydration process at the early stage when the paste is very weak. Second, drying and vacuuming will cause a distortion of the fragile microstructure. Third, the in situ continuous monitoring of the chemical compositions and morphology can't be achieved by using SEM. In order to overcome the defects of SEM, an advanced microscopy technique—environmental scanning electron microscope (ESEM) has been developed in recent years with a capability of in situ continuously observing the reaction process in an 'environment' atmosphere. ESEM has the following characteristics in comparison with the common SEM [9–15]:

(1) Sample preparation is very simple and convenient. Drying and coating treatments are not essential. Freshly mixed sample or hardened paste can be directly placed into the 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.

Table 2
Chemical compositions of metakaolin

Raw materials	SiO_2	Al_2O_3	Fe_2O_3	CaO	TiO_2	MnO	K_2O	P_2O_5	L.O.I
Metakaolin	62.97	26.91	2.62	0.60	1.24	0.01	0.18	0.74	4.44

These functions make it possible to follow the micrograph changes of hydration products with time at the same location during the early age of the hydration process under a moist environment. In addition, by means of EDXA as supplementary equipment, ESEM can quantitatively identify the changes in chemical compositions on the surface of the samples, thus providing a further scientific insight into the reaction mechanism.

The authors have investigated the hydration process of K-PS and K-PSDS geopolymeric cement pastes using ESEM, and published the experimental results [16,17]. This paper presents some researches into the hydration process of K-PSS geopolymeric cement paste. In this study, the changes with time in the micrographs and chemical compositions at the same location were monitored and recorded for K-PSS geopolymeric bulk paste by using ESEM and EDXA. The monitored period started from 10 min after mixing, and ended at 13 h when 80% of the final strength has been 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. The chemical composition of metakaolin is listed in Table 2. 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 the experiment.

2.2. Methods

2.2.1. Mixture proportion and sample preparation

In this study, KOH, potassium silicate solution and water were mixed first in a beaker and cooled to room temperature, and then metakaolin powder was added into the cooled alkaline solution and mixed for 3 min by hand. After that, the fresh geopolymeric cement paste was rapidly poured into a steel sample holder. The

Table 3
Mixture proportions and compressive strength of K-PSS geopolymer

Oxidants ratio of K-PSS geopolymeric cement (M/M)			Solid to liquid ratio	Compressive strength (MPa)					
SiO_2/Al_2O_3	K_2O/Al_2O_3	H_2O/K_2O		6 h	9 h	13 h	24 h	3 d	28 d
4.5	0.8	5.0	0.6	16.3	27.1	28.2	28.5	31.6	34.7