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Long-term Durability of Cement-based Materials with Very Low *w/b*

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Abstract: To investigate the durability, especially the long-term stability of cement-based materials with very low *w/b*, the air permeability test, carbonation test, capillary absorption rate test and dilation potential test were adopted under long-term heat treatment condition. Microstructure of these materials is also analyzed by scanning electronic microscopy (SEM) and mercury intrusion porosimeter (MIP) in order to further unveil its mechanism and interrelation between microstructure and its properties. The results indicate that in the area investigated, cement-based material with *w/b* 0.17, like RPC, possesses low porosity and excellent durability. Moreover, its porosity will further decrease under long-term heat treatment compared with normal heat treatment. Its long-term durability is much superior to that of other cement-based materials with *w/b* 0.25 or 0.35 as high strength concrete(HSC).

Key words: cement-based material; durability; dilatability potential; air permeability; carbonation;capillary absorption

1 Introduction

Durability of cement-based composites is very important to extend the service life of concrete buildings and to save its maintenance costs. However, it is a very complicated problem because the durability is affected by many factors such as the composition of raw materials, mix proportion and environmental conditions[1-5]. The most difficult is a long age is needed for durability research, which cannot be covered in laboratory condition. Therefore, little systematic knowledge related to the long-term durability of cementitious materials has been obtained. In the past decade, researchers placed an emphasis on the high strength/performance concrete with low *w/b*, containing reactive mineral powder and a high range water reducing agent. Recently, a kind of very high strength concrete such as reactive powder concrete(RPC) with a high amount of silica fume and *w/b* lower than 0.2 was developed[6-8]. According to the cement hydration theory, there must be numerous unhydrated cement particles and reactive mineral powders in these materials. If water can be supplied from external environment, unhydrated particles in cement-based material with low *w/b* will continue to hydrate, causing an expansion in volume of hydration products, which probably results in damage of concrete microstructure. However, ingress of the external water into the interior of cement-based materials is difficult due to its dense microstructure with a very low porosity[8]. Hence, it is difficult to determine whether unhydrated particles in cement-based materials with low *w/b* are chemically stable or not. It is also unknown that whether the long-term durability of cement-based materials with low *w/b* is affected by these unhydrated particles or not. Moreover, little systematic research related to this has been carried out and few reliable methods have been employed to study the long-term performance of this cementitious material by now. Therefore, to further study the long-term durability of these advanced cement-based materials will be helpful to understand the relationships between composition, microstructure and performance of high/ultrahigh strength cement-based materials and to develop more advanced cement-based materials.

Previously, some information related to above questions was documented[9-12], which provided the basis for further study on this question. Some researchers observed that the polished surface of the specimen with *w/b* of 0.30 will generate cracks when subjected to 90 ℃ water treatment[11]. It is obvious that the hydration reaction between cement particles and water will proceed if there are unhydrated cement particles in the observed surface because the reactive unhydrated cement clinkers particle comes directly in contact with water. The hydration products will extend to free polished surface direction, resulting in external surface cracks. However, for unpolished specimens, the author questions that they will crack under the same

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curing conditions because the unhydrated particles are surrounded by a dense hydration products layer and are not directly exposed to water in the same manner. Whether the unhydrated particles hydrate or not and the extent unhydrated particles hydrate depends on the ingress of external water into interior to contact with particles.

2 Experimental

2.1 Raw materials

Grade 52.5 ordinary Portland cement in conformance with Chinese standard GB175-1999 with 54.5 MPa compressive strength at 28 d is used. It was made by Jingyang cement factory, and abbreviated as C. Silica fume used is from the Elkem Co. of Norway and is denoted as SF. The granulated blast furnace slag used, abbreviated as PS, is from Baoshan Steel Lt. Co. in Shanghai City. The fly ash produced by Nantong Power Plant in Jiangsu Province, denoted as FA, is used. The chemical composition and physical properties of cement, silica fume, slag and fly ash are given in Table 1. The mean size of the raw material was measured using LS230 laser separator-size analyzer. A naphthalene sulfonic acid formaldehyde condensation product made by Shanghai Huawang Chemistry Company, denoted as SP, was added into the mixtures in order to make the specimens obtain the expected flowability.

The quartz sand with a specific gravity of 2.70 was used as aggregate for preparation of mortar specimen. Its size distribution is 0.08-1.25 mm and its fineness modulus is 2.2.

2.2 Preparation of specimens

In order to determine the long-term durability of cement-based material with low *w/b*, five series of mortar specimens were designed. Their compositions were listed in Table 2. All samples were fabricated using stainless steel molds with specified dimensions. These samples were demolded at 1 d after cast. Then corresponding curing was carried out. Standard curing procedure is that sample is cured in water with a temperature of (20±2) ℃ after demolded. (Normal) Heat treatment curing condition is defined as specimen cured for 3 d in water with a temperature of (20± 2) ℃ after demolded and then cured in water with a temperature of 90 ℃ for another 3 d.

2.3 Methods

Rapid carbonation test method (Chinese standard GBJ82-85) is used as carbonation test of mortar sample in this paper. The carbonation test is performed at 28 d age and the time-span of carbonation is 56 d. Cylinder sample with a dimension of ∅150 mm×50 mm and nitrogen gas are used for gas permeability test. All specimens are placed into a box at 105 ℃ to dry for 48 h before their carbonation test and gas permeability test.

Gas permeability coefficient K is calculated using Equation (1).

$$K = \frac{2QP_0L\eta}{A\left(P^2 - P_0^2\right)} \quad (1)$$

Where Q is flow velocity of gas; L is the distance through which gas flows; A is the cross section area of the specimen; P denotes the absolute pressure between the top and the bottom of specimen. P_0 is the atmospheric pressure; η is the gas dynamic viscosity coefficient. All units for the above parameters are given as international units. The average value for three specimens is taken as the final gas permeability coefficient. The unit of K is m^2.

The capillary absorption test is performed on the basis of the methods presented in reference[13]. The details are as followings: The specimen is demolded at 1 d after casting. Then some specimens undergo specified curing treatment. It is cured first in water with temperature (20±2) ℃ for 3 d ,then treated in 90 ℃ water for 3 d. The other specimen is directly kept in (20 ±2) ℃ water after demolded till specified ages. When curing is finished, the specimen with dimension of 40 mm×40 mm×160 mm is taken out from the water and

Table 1 Mean diameter and oxide composition of cement and reactive powders

Item	Composition /wt%							Mean diameter	Specific
Raw materials	SiO_2	Al_2O_3	CaO	MgO	Fe_2O_3	SO_3	K_2O	/ μ m	gravity
C	21.7	5.2	64.2	1.0	2.7	3.4	0.7	18.9	3.15
PS	34.3	15.1	39.6	6.0	0.8	0.7	-	7.1	2.75
FA	57.6	30.8	3.0	1.5	5.8	1.3	-	9.8	2.40
SF	96.1	0.5	0.3	0.6	0.5	1.3	0.5	0.2	2.15

Table 2 Mix proportion of raw materials of samples / (kg/m^3)

Serials	C	PS	FA	SF	SP	Aggregate	Water (*w/b*)
M1	613	0	255	153	20.4	1225	174 (0.17)
M2	613	255	0	153	20.4	1225	174 (0.17)
M3	575	240	0	144	9.6	1150	240(0.25)
M4	550	228	0	137	8.7	1103	320(0.35)
M5	580	380	0	0	9.7	1160	240(0.25)

Note: *w/b* means water to binder(cement, PS, FA or SF) ratio.

the excess water is removed from its surface. Then, recording the initial weight G_0 of specimen, curing it at 105 ℃ for 48 h, and recording the weight G again after cooling it in a desiccator. Hence, we can get the total loss of weight (G_0-G). After that, specimens are placed in (20±2) ℃ water again, the increase in weight of sample with time up to 48 h is determined. The capillary absorption rate is calculated by dividing the weight of absorbed water of specimen during a chosen time by its total weight loss (G_0-G) for its corresponding ages.

The dilation potential is determined by measuring length change of mortar samples. The dimension of specimen is 30 mm×30 mm×280 mm. Stainless copper-alloy nailhead is pre-placed in two sides of specimen when cast. Demolded at 1 d after casting, the specimen is sealed by films and placed in a box at (20±2)℃ for 27 d to cause self-desiccation. Then, initial length is measured by micrometer caliper and the specimen is again moved into the curing room to cure under a specified condition and the length of specimen at corresponding ages is recorded. The difference value between two ages is calculated and the dilation for corresponding ages can be obtained. The testing detail is referred to ASTM C596-89.

In order to better know the information about the long-term durability of cementitious materials with low *w/b,* the sample is first sealed by two layers plastic membrane designedly in order to generate a serve self-desiccation effect within system and therefore pre-introduce some defects before the dilation potential test.

When the dilation potential test is finished, pieces of specimen from test sample are chosen to carry out the MIP and SEM experiments.

3 Results and Discussion

3.1 Gas permeability and carbonation

The results of gas permeability of four samples subjected to two curing conditions are shown in Table 3. It can be found that, under two curing conditions, the gas permeability of four samples is very low. However, the most noteworthy is that the gas permeability of sample with *w/b* 0.17 denoted as serial M2 is much lower than that of other three. This indicates that it is much more difficult for gas to pass through serial M2 sample than through the other three samples. The smaller the *w/b* of sample is, the lower the gas permeation coefficient is. Meanwhile, one can observe that the curing conditions can also affect the gas permeability of samples. The gas permeability of the sample exposed to the heat treatment condition is low compared with normal curing.

From the results of carbonation test shown in Table 3, it can be seen that the carbonation of the four samples is not detected. In fact, it is reasonable because the permeabilities of four samples are too low for CO_2 to ingress into interior of sample. The result of the carbonation test is consistent with the result of gas permeability of specimen.

3.2 Capillary absorption

In this work, the total weight loss of samples by drying is measured to determine capillary water absorption. According to the results shown in Table 4, the total weight loss of serial M2 sample and serials M3 sample decreases with the increasing curing age. However, the total weight loss of serial M5 sample in 28 d is larger than that in 3 d. And under heat treatment condition, the total weight loss of serial M5 sample is as same as that of serial M3 sample. This results from the characteristics of mixing proportion of the same *w/b* and different compositions in raw materials of serial M3 sample and serial M5 sample.

In addition, the total weight loss of serial M2 sample is much less than those of serial M3 sample and serial M5 sample. And one can also notice that, by heat treatment, the total weight loss of the sample further decreases compared with the normally cured sample. The most remarkable observation is that under the three curing conditions the total weight losses of serial M2 sample are all less than 2%. Especially for the heat treatment condition, the total weight loss of serial M2 sample is only 0.4%. These results suggest that the increase of hydration products reduces the capillary pore with increasing age and consequently decreases the amount of free water in the capillaries. The employment of heat treatment speeds the hydration reaction and further decreases the capillary pore space of the sample.

The experimental results of capillary absorption rate of specimens are given in Fig.1-Fig.3. For the serial M2 sample and serial M3 sample, one can see that the sample with long age shows low capillary absorption rate during all absorption times. Also, the capillary absorption rate of sample with lower *w/b* is lower than that of specimen with higher *w/b*. And especially for the sample treated by 90 ℃ water, its capillary absorption rate is very low. Furthermore, the capillary absorption rate in the first 1-2 hours increase rapidly; then the capillary absorption rate is almost constant. However, the capillary absorption rate of serial M5 sample is almost same under three curing conditions. And the capillary absorption rate of serial M5 sample

Table 3 Experimental results of carbonation and gas permeability of specimens

Series	Curing conditions	Carbonation depth /mm	Gas permeability /$\times10^{-18}$m^2
M2	Standard curing, 28 d	0	3.81
	Heat treatment	0	3.12
M3	Standard curing, 28 d	0	112.0
	Heat treatment	0	57.7
M4	Standard curing, 28 d	0	-
	Heat treatment	0	106.2
M5	Standard curing, 28 d	0	-
	Heat treatment	0	71.5

Table4 Total weight loss of various water-saturated systems after 2 d of drying at 105 ℃

Series	Curing condition	The total loss of weight /%
M2	Standard curing, 3 d	1.7
	Standard curing, 28 d	1.4
	Heat treatment	0.4
M3	Standard curing, 3 d	6.1
	Standard curing, 28 d	4.6
	Heat treatment	2.4
M5	Standard curing, 3 d	4.9
	Standard curing, 28 d	6.2
	Heat treatment	2.4

is much lager than that of serial M2 sample. This indicates the serial M5 sample is easier to absorb water than other three samples. The capillary absorption rate largely depends on the capillary space of the hydrated sample[13]. From the capillary absorption results, it follows that there is very little or almost no capillary pore space in cement-based materials with very low *w/b* such as serial M2 sample with *w/b* 0.17.

3.3 Dilation potential under long-term heat treatment.

Fig.4 gives the results of the dilation potential tests of samples under long-term heat treatment condition. The long-term heat treatment procedure is shown in Fig.4.The results shown in Fig.4 indicate that the dilation of the four samples (serial M1, M2, M3 and M4) with different *w/b* obviously differ from each other. Whether cured under 20 ℃ water or 90 ℃ water condition, serial M4 sample expands up to about 200 μm/m when 87 days curing age completes. The serial M3 sample shows the same tendency as serial M4 sample, its expansion ratio reaches about 100 μm/m when 87 days curing age completes.

The serial M1 and M2 samples with *w/b* 0.17 actually shrink during the first heat treatment stage with 90 ℃ water (for 9 d) and reaches a same shrinkage value of about 120 μm/m. And when it is placed in 20 ℃ water again, length of the serial M2 sample remains almost constant till about 30 days age and then recovers to the initial level (no shrinkage and no expansion) at about 75 days age. The most interesting thing is that, during the second heat treatment stage of 12 d, the serial M2 specimen firstly shrinks again and then expands and finally keeps its expansion ratio constant at about 10 μm/m. The serial M1 sample shows the same tendency as serial M2 sample. However, it shows

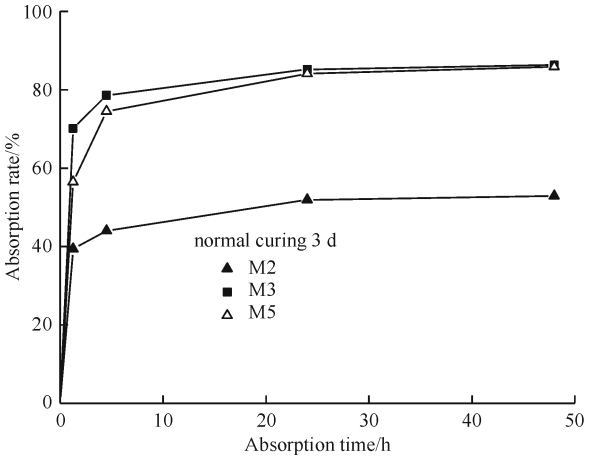


Fig. 1 Capillary absorption water rate at 3 d age of various samples

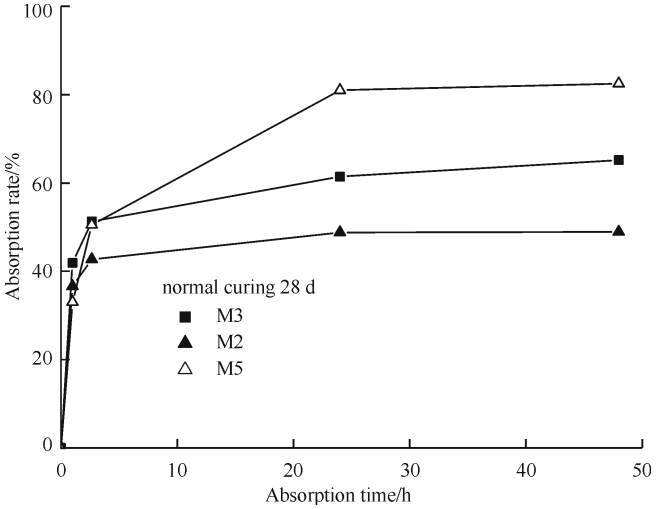


Fig. 2 Capillary absorption water rate at 28 d age of various samples

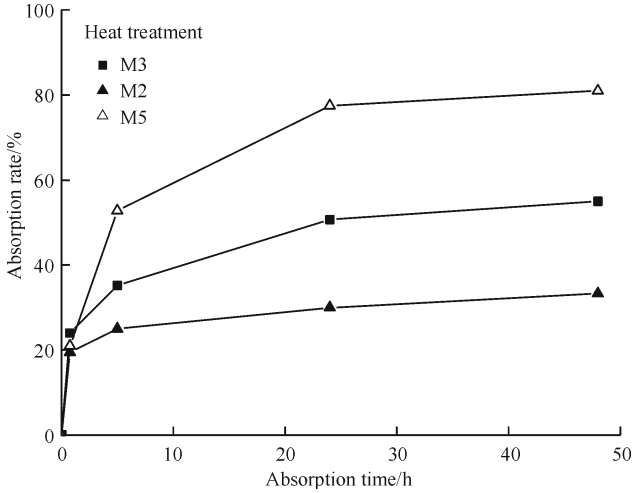


Fig.3 Capillary absorption water rate of various samples under heat treatment

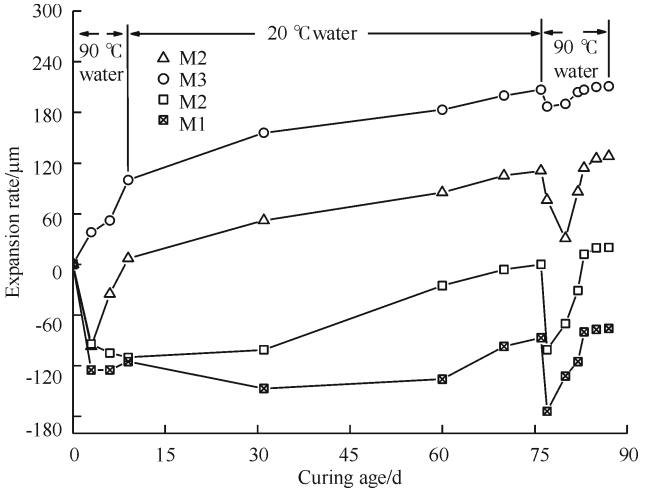


Fig.4 Potential expansion rate of specimens subjected to long-term heat treatment condition

a shrinkage strain value of about 100 μm/m in the end when 87 days curing treatment finishes.

The above results imply that, under long-term curing conditions presented in this paper, the expanding-effect in cement-based materials with *w/b* 0.17, especially for serials M1 sample with FA, is almost not observed. This indicates that ingress of water from external environment into interior of cement-based material with *w/b* 0.17 is very difficult. And the unhyrated reactive particle in cement-based materials with very low *w/b* is probably stable and is very difficult to hydrate. The long-term performance of cement-based material with *w/b* 0.17 is much better than the two other samples with lager *w/b*. However, the long-term durability of serial M3 samples and serial M4 sample with larger *w/b* is probably iffy since they can cause a high expansion ratio under investigated curing conditions.

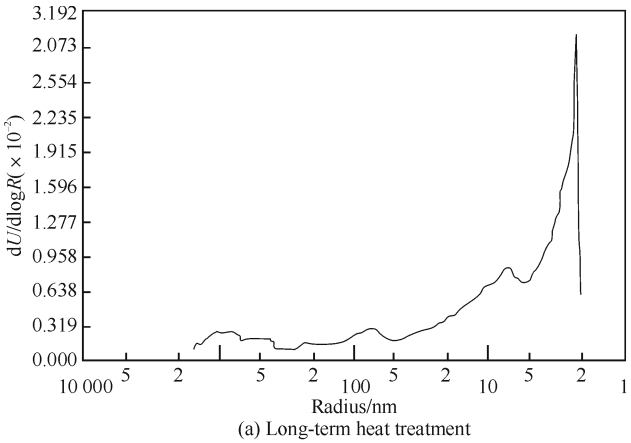
As to the variation in length of sample with various *w/b* and various compositions of raw materials subjected to long term heat treatment, it is considered that this may be a consequence caused by many complicated reasons. For the serial M3 and M4 samples, water is easier to penetrate into its interior due to its looser microstructure compared to serial M1 and M2 samples, which probably causes unhydrated particle to continue to hydrate and leads to a high expansion in volume. And also, the delayed ettringite formation may be another reason for its expansion under this experimental condition. However, though the serial M1 and M2 samples have a dense microstructure and ingress of external water into its interior is very difficult, the long-term heat treatment may bring a force to make residual water in interior further consume by hydrating, which probably result in shrinkage in length and also make its microstructure further dense. It appears similar to "self-dessication effect".

3.4 Microstructure of sample treated by long-term heat treatment

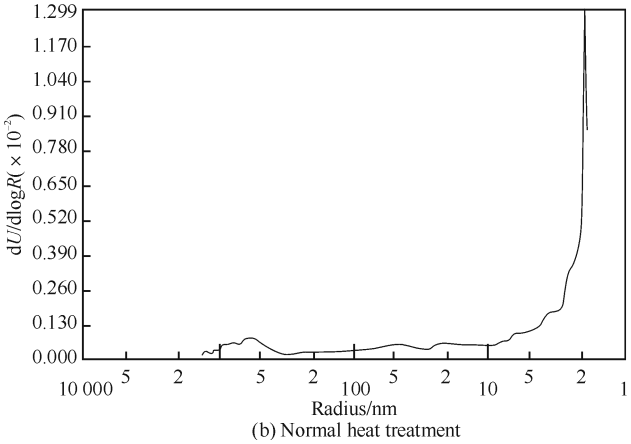
From above result, one can find that the investigated samples with different *w/b* have very low gas permeability and no carbonation. However, the results of dilation potential test for the four samples greatly differ from each other. In order to better understand the results and clarify the relationship between microstructure and performance of samples exposed to long-time heat treatment, Mercury intrusion porosity (MIP) and scanning electron microscopy (SEM) were employed to study the microstructure of the samples in this section. The results are shown in Fig.5-Fig.6.

3.4.1 Mercury intrusion porosity (MIP)

It can be seen that, from the result given in Fig.5, the differential curves of porosity of serial M2 samples under two curing conditions are almost the same. The mode radiuses of pore of samples with two curing conditions are 2.1 nm and 2.2 nm, respectively. The test results also show the porosity of samples subjected to long-term heat treatment for 21 d and normal heat treatment (90 ℃ water for 3 d) are 1.07% and 2.23 %, respectively. This indicates that, under the long-term

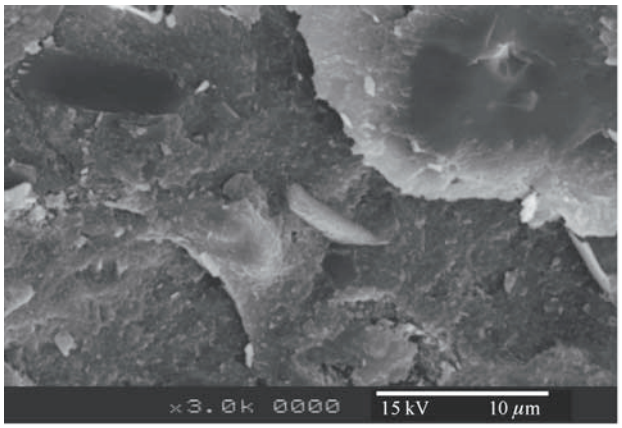


(a) Long-term heat treatment

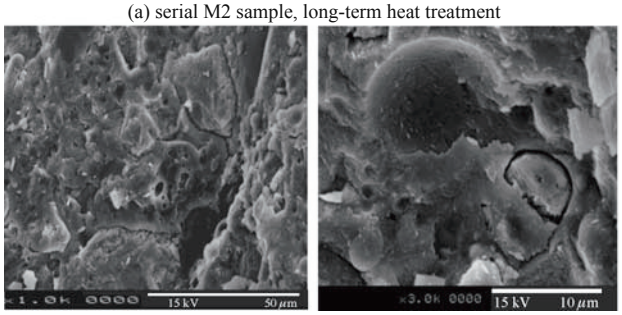


(b) Normal heat treatment

Fig. 5 Porosity and pore size distribution of serial M2 sample under various conditions



(a) serial M2 sample, long-term heat treatment



(b)serial M4 sample, long-term heat treatment

Fig.6 SEM pictures of serial M2 and M4 samples subjected to long-term heat treatment

heat treatment condition, the porosity of cement-based material with *w/b* 0.17 remarkably decreases and its mode radius of pore almost keeps constant compared with the sample exposed to the normal heat treatment condition. Because a high amount of SF and PS containing in serial M2 sample brings fully into play pozzolanic effect and filler-effect under long-term heat treatment, the further improvement in its pore structure makes external water more difficult to enter into the interior, resulting in a good long-term durability.

3.4.2 SEM

The SEM pictures of serial M2 sample and serial M4 sample under the long-term heat treatment conditions are shown in Fig.6. From the photo given in Fig.6, one can find that the microstructure of serial M2 sample is dense and homogenous. However, the specimen denoted as serial M4 possesses loose and inhomogenous microstructure containing some cracks. This may result from that under long term heat treatment condition, excess external water ingress into internal microstructure of serial M4 sample due to its more porosity and cause the unhydrated cement clinker particles and unhydrated PS and SF particles continue hydration. Therefore, more hydration products are produced, which results in damage of microstructure of sample.

The improvement of the microstructure of sample resulting in low water to binder ratio and addition of mineral mixture such as PS and SF as well as employment of heat treatment may be responsible for its excellent long-term durability.

4 Conclusions

a)The gas permeability of cement-based materials with *w/b* 0.17, such as RPC, is very low and resistance to carbonation. Its capillary porosity and capillary water uptake are very small or is negligible.

b) Compared with cement-based materials with *w/b* of 0.25, 0.35 (serial M3, M4 and M5 sample), the long-term durability of cement-based materials with *w/b* less then 0.2 such as *w/b*=0.17 (serial M1 and M2 sample) is much better.

c) The results of MIP and SEM indicate that cement-based material with *w/b* 0.17 such as RPC and a high amount reactive mineral powders possesses a dense microstructure and very low porosity under 90 ℃ water for long time(21 d) curing condition.

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