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预水化对水泥性能及水泥-聚羧酸系减水剂相互作用的影响

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摘　要：将新鲜的硅酸盐水泥暴露于(20±2) ℃，相对湿度为 85%~90%的环境中，研究了硅酸盐水泥因暴露于湿空气中产生预水化而对水泥标准稠度用水量、水泥水化行为、水泥胶砂强度以及水泥与聚羧酸系减水剂(PCE)间相互作用的影响。结果表明：随着暴露时间的增长，水泥预水化速率不断降低，标准稠度用水量则先轻微减小后显著增加，预水化 4 d 的水泥具有最小的标准稠度用水量；预水化作用总体上降低了水泥水化温峰值及水泥水化放热速率，但对于预水化作用不超过 10 d 的水泥。在其水化 200~500 min 期间，预水化水泥的水化放热速率随预水化时间的延长而增大，对于预水化 10 d 的水泥，其水化放热速率甚至一度高于新鲜水泥，这可能会导致预水化水泥的异常凝结。此外，预水化作用不利于胶砂强度的发展，且对抗折强度的不利影响尤为显著。预水化作用还会影响 PCE 的分散效果，随着预水化时间的延长，PCE 的分散性及其分散保持性先增大后减小，对预水化 4 d 的水泥分散效果最佳，其初始流动度达到新鲜水泥的 136%，且 120 min 后的浆体流动度仍高达 235 mm。PCE 对预水化 20 d 和 30 d 的水泥无分散效果。

关键词：预水化；陈化；水泥水化；水泥胶砂强度；聚羧酸系减水剂
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Effect of Prehydration on Properties of Cement and Interaction Between Prehydrated Cement and Polycarboxylate Superplasticizer

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Abstract: Fresh Portland cement was exposed to the specific conditions of (20±2) ℃ and 85%–90% relative humidity. Effect of prehydration on the water requirement of normal consistency of cement, the cement hydration behavior and the development of mortar strength at different exposure time was investigated. The interaction between prehydrated cement and polycarboxylate superplasticizer (PCE) was also assessed. The results show that the prehydration rate decreases with increasing the exposure time. However, the water requirement of normal consistency decreases firstly and then increases rapidly as the growth of exposure time due to prehydration. Meanwhile, prehydrated cement for 4 d exposure has the smallest water requirement of normal consistency. The prehydrated cements exhibit a lower value of highest hydration temperature and a lower exothermic rate than fresh cement. The exothermic rate of cement increases with increasing the exposure time when the exposure time is less than 10 d. The cement for 10 d exposure even has a greater exothermic rate rather than fresh cement sample. This phenomenon can lead to an abnormal setting behavior of prehydrated cement. In addition, prehydration can affect the strength development especially the flexural strength development of mortar. Prehydration also influences the effectiveness of PCE, the dispersion ability and dispersion retention ability of PCE increases firstly and then decreases as the increasing of exposure time. PCE in the paste of prehydrated cement exposed for 4 d exhibit the best dispersion and dispersion retention ability. Its initial fluidity is 136% of that for fresh cement paste, and its fluidity still remains at 235 mm after 120 min. However, PCE lost its dispersion ability to cement exposed for 20 d and 30 d.

Keywords: prehydration; aging; cement hydration; strength of cement mortar; polycarboxylate superplasticizer

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1 Introduction

Cement reacts with water vapour readily during production, transport and subsequent storage due to its susceptibility to moisture.[1–2] This process usually uses the term "prehydration" to refer to all the processes that cause unintentional loss of reactivity prior to the usual mixing of cement with water.[3–4] Dubina, *et al.*[5] used dynamic vapour sorption to ascertain the prehydration thresholds of various cement clinker phases. Their results showed that CaO and C_3A are rather reactive toward water vapour whereas the silicates react less. Vektaris, *et al.*[6] obtained the similar conclusion that white cement is more resistant to prehydration compared to Portland cement because it contains less C_3A, C_4AF and alkali. Therefore, cement with a higher level of CaO and C_3A is particularly sensitive to moisture and may cause properties fluctuation of cement, which could be highly stressed.

In a practical application, cement may be used soon after production in the peak period of construction or may be stored for several months before usage in the depression period. For cement-based products, like dry-mix mortars, are usually stored in bags that are permeable to air. Therefore, prehydration is unavoidable during long period storage and may be serious in a high air humidity environment of the southern China. Superplasticizers, like polycarboxylate superplasticizer (PCE), are widely used in the cement-based products due to their outstanding water-reducing rate. PCE is sensitive to cement properties change. It is thus important to investigate the effect of prehydration on the change of cement properties, which causes the incompatibility phenomenon between prehydrated cement and PCE.

In this paper, the changes of water requirement of normal consistency, the cement hydration behavior and the development of mortar strength at (20±2) ℃ and 85%–90% relative humidity were investigated. The initial fluidity and time-depended fluidity loss of cement paste were examined to evaluate the interaction between prehydrated cement and PCE.

2 Experimental

2.1 Materials

Fresh P·Ⅰ42.5 Portland cement (GB 8076—2008, China) was used when it was fresh. The cement was sealed with plastic bags and stored in bucket. The reference sand was provided by Xiamen ISO Standard Sand Co., Ltd. The preparation procedure for the PCE used can be referred in a Ref. [7].

The reference sand was used and a self-prepared PCE with a solid content of 40% was chosen.

2.2 Methods

To establish the adsorption amounts of water vapour and CO_2 as a function of time, 100 g cement was put into a pre-weighted plastic cup. The experiments were carried out at relative humidity of air of 85%–90% and room temperature of (20±2) ℃. The prehydrated cement samples were ground and then sieved by a sieve with the square holes of 0.9 mm before they were used in further experiments due to the lump formation during exposure period.

The water requirement of normal consistency of cement, and the development of mortar strength were measured according to the methods specified by GB/T 1346—2011 and GB/T17671—1999, respectively. For mortar strength measurement, the mix mass proportion of mortar was 1.0(cement):3.0(sand): 0.5(water), and all the mortar samples were firstly cured in 90% RH(relative humidity) for 24 h and then moved into water for 2, 6 and 27 d under the curing condition based on the GB/T 17671—1999.

The temperature of cement hydration was measured during the cement hydration and the relation between temperature *versus* time was plotted. The hydration heat and exothermic rate can be calculated based on GB/T 12959—2008.[8–9] The water-to-cement ratio was 0.35 and 60 g cement paste was placed into a thermos cup in a thermostatic bath at 25 ℃. A temperature probe was dipped into the paste immediately and the temperature of the paste was continuously recorded by a digital thermometer. The time interval was 1 min.

The effect of prehydration on the interaction between prehydrated cement and PCE was characterized *via* the measurement of the fluidity as a function of time. All the experiments were carried out at PCE dosage of 0.12% based on cement mass and water-to-cement ratio of 0.26. The measurement method was used according to GB/T 8077—2012.

3 Results and discussion

3.1 Prehydration rate of cement

Figure 1 shows the mass increment of cement as a function of exposure time and the related fitting equation. The slope change illustrates that the mass growth rate gradually decreases with exposure time. A rapid prehydration of sensitive mineral phases, like aluminate and ferrite, occurs during exposure period.

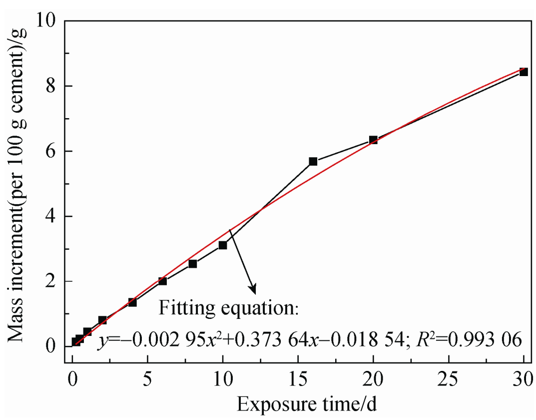


Fig. 1 Mass increment of cement as a function of exposure time

3.2 Water requirement of normal consistency

Figure 2 shows the effect of exposure time on the water requirement of normal consistency. The water requirement of normal consistency slightly decreases when the exposure time is not more than 4 d. After that, the water requirement of normal consistency increases rapidly. The possible reason is due to the rapid consumption of aluminate and ferrite, which are more sensitive to moisture than silicate. [5] Meanwhile, the formation of hydrates on the cement particle surface causes the increment of internal specific surface area (S_{BET}),[1] which consequently follows that more water is needed to achieve paste of normal consistency.

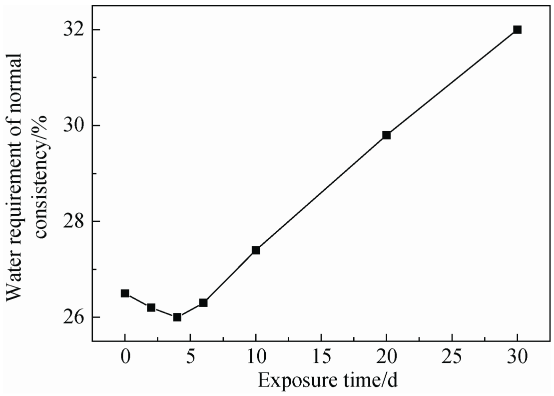


Fig. 2 Effect of exposure time on the water requirement of normal consistency

3.3 Cement hydration behavior

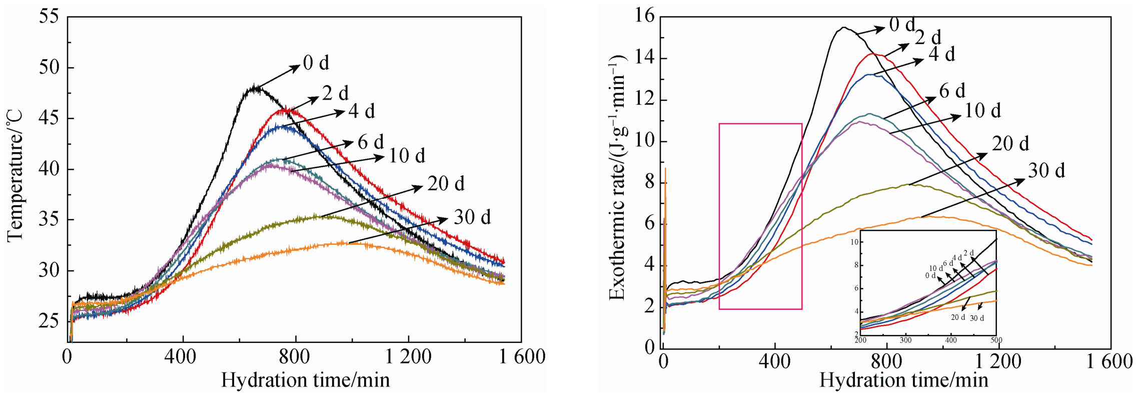
Figure 3 shows the hydration temperature raise and exothermic rate as functions of exposure time for different cement samples. In Fig. 3(a), the prehydrated cement samples exhibit a significantly lower value of highest hydration temperature than the fresh cement sample. The longer the exposure time, the lower the maximum hydration temperature will be. This can be determined as the partial surface hydration during the process of exposure. [1]

In Fig. 3(b), the exothermic rate of fresh cement sample is greater than the exothermic rate of prehydrated cement samples when hydration time is not more than 200 min. However, for prehydrated cement samples when the hydration time ranges from 200 to 500 min, the longer the exposure time is, the greater the exothermic rate will be. The cement sample with 10 d exposure even has a greater exothermic rate than fresh cement sample (see Fig. 3(b)). This phenomenon is unclear because it is closely related to the setting behavior of cement.

3.4 Development of mortar strength

Prehydration can reduce cement reactivity and affect the development of strength. Table 1 shows the effect of exposure time on the development of flexural and compressive strengths of mortar.

Table 1 shows that prehydration can degrade the flexural strength of mortar significantly even when the exposure time is only 2 d. Meanwhile, the flexural strength loss ratio of mortar gradually increases when the exposure time prolongs. The flexural strength loss ratio cannot be recovered well even with prolonging the curing time when the exposure time is less than 6 d. However, the flexural strength loss ratio can be recovered in some extent when exposure time is over 10 d.



(a) Temperature rise　　　　(b) Exotherimic rate

Fig. 3 Effects of exposure time on the temperature rise and exothermic rate of cement samples

Table 1 Effect of exposure time on the development of mortar strength

Sample	Flexural strength/MPa			Strength loss ratio/%			Compressive strength/MPa			Strength loss ratio/%		
No.	3 d	7 d	28 d	3 d	7 d	28 d	3 d	7 d	28 d	3 d	7 d	28 d
M-0	6.6	8.8	9.7	0	0	0	28.8	38.7	49.5	0	0	0
M-2	6.0	7.8	8.6	9.1	11.4	11.3	23.4	33.8	45.9	18.8	12.7	7.3
M-4	5.9	7.8	8.7	10.6	11.4	10.3	22.8	34.1	46.2	20.8	11.9	6.7
M-6	5.4	7.5	8.1	18.2	14.8	16.5	22.1	31.4	45.8	23.3	18.9	7.5
M-10	5.0	7.0	8.1	24.2	20.4	16.5	20.0	29.6	42.1	30.6	23.5	14.9
M-20	3.7/	6.5	7.7	43.9	26.1	20.6	14.8	23.5	39.2	48.6	39.3	20.8
M-30	2.4	4.2	6.4	63.6	52.3	35.0	8.3	14.7	29.0	71.2	62.0	41.4

"M-*" means cement mortar is prepared by using the cement which is exposed for "*" days.

For the compressive strength of mortar, the compressive strength loss ratio gradually increases with the increase of exposure time. This result is similar to the flexural strength loss ratio change. Also, the compressive strength degradation degree of mortar is more serious than the flexural strength degradation degree of mortar when the curing time is less than 7 d. However, the compressive strength loss ratio can be recovered when the curing time is prolonged. The compressive strength loss ratio can be recovered from 18.8%–23.3% (when the curing time is 3 d) to 6.7%–7.5% (when the curing time is 28 d) at the exposure time of less than 6 d.

3.5 Effectiveness of PCE

Table 2 shows that the PCE exhibits greater dispersing ability and dispersion retention ability in prehydrated cements (when the exposure time is less than 10 d), compared to fresh cement. It can be determined as a PCE-consuming component (like C_3A) content of prehydrated cement, which is lower than that of fresh cement. Prehydrated cement consumes less PCE than fresh cement. Therefore, there are more PCE molecules for dispersion in prehydared cement paste rather than in fresh cement paste. In addition, the fluidity and fluidity loss behavior of the group "P-4" appear optimum. When the exposure time is more than 4 d, the effectiveness of PCE begins to degrade. Moreover, the pastes will become too stiff to measure when the exposure time is more than 10 d. This tendency is consistent with the change of the water requirement of normal consistency (see Fig. 2). The reason is that the hydrates generated during the exposure process (such as C-S-H) cause the increment of internal specific surface area.

Table 2 Effects of exposure time on effectiveness of PCE

Sample No.	Fluidity/mm			
	5 min	40 min	80 min	120 min
P-0	225	145	90	
P-0.25	245	145	90	
P-0.50	270	175	105	
P-1	290	205	140	
P-2	300	275	245	175
P-4	305	295	280	235
P-6	300	285	275	225
P-10	290	275	215	140

"P-*" means cement paste is prepared by using the cement which is exposed for "*" days; P-20 and P-30 pastes were too stiff to measure.

4 Conclusions

1) Prehydration could firstly decrease and then increase the water requirement of normal consistency as the exposure time increased. The reason was that the hydrates generated during the exposure process, like C-S-H, caused the increment of internal specific surface area.

2) Prehydration caused the change of hydration behavior of cement. The effectiveness of chemical admixtures used in prehydrated cement could be tested before practical application for ensuring the safety use of chemical admixtures.

3) Prehydration could reduce cement reactivity and affect the development of flexural strength and compressive strength. The flexural strength loss ratio could not recover well while the compressive strength loss ratio could recover greatly as a result of extended curing time.

4) PCE exhibited a greater effectiveness in slightly prehydrated cement than in fresh cement due to the lower PCE-consuming component content of prehydrated cement.

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