RELEASE OF Na^+ AND K^+ IONS IN CEMENT PASTES INCORPORATED WITH FLY ASHES IN DE-IONIZED WATER

Deng Min[1,2*], Liu Bin[3], Xu Lingling[1], Mo Liwu[1], Tang Mingshu[1,2]

[1] College of Materials and Engineering, Nanjing University of Technology, Jiangsu 210009, P.R. China

[2] State Key Laboratory of Materials-Oriented Chemical Engineering, Nanjing, Jiangsu 210009, P.R. China

[3] China Construction Ready Mixed Concrete Co., Ltd, Wuhan, Hubei 430074, P.R. China

Abstract

Cement pastes incorporated with 0%, 20%, 35% and 50% of fly ashes by weight were prepared. After 90d of curing, the cement pastes were crushed and ground into powders with a particle size less than 0.080mm, and then the powders were soaked in de-ionized water. The contents of Na^+ and K^+ ions in the water were measured. Results show that the K^+ and Na^+ ions in cement pastes enter rapidly into the de-ionized water during the first 120 minutes, and then were released by cement pastes at a relatively slow rate. An equilibrium between the release and absorption of K^+ and Na^+ ions by cement pastes was reached at approximately 720 minutes. Releasable alkali contents were 74%, 76%, 70% and 63% for cement pastes contained 0%, 20%, 35% and 50% of fly ashes and cured for 90 days. No significant effect of fly ash on the retaining of available alkalies on solids of cement pastes was observed. These releasable alkali ions may exist in bulk pore solutions or be physically absorbed by solids of cement pastes.

Keywords: release, K^+, Na^+, cement pastes, fly ashes

1. INTRODUCTION

Alkali-silica reactive aggregates are widely distributed and alkali-silica reaction has caused some deteriorations of concrete all over the world [1]. It is generally accepted that sufficient amount of fly ashes may effectively decrease expansion due to alkali-silica reaction [2]. Incorporation of fly ashes in

*Correspondence to: dengmin@njut.edu.cn

concrete is one of main measures to combat alkali-silica reaction of cement concrete [3]. Inhibiting effect of fly ashes on alkali-silica reaction is mainly contributed to the lower alkalinity of pore solutions by the dilution of fly ashes to available alkalies and stronger adsorption of alkali ions by C-S-H gels with a lower Ca/Si formed by blends of OPC and fly ashes [4,5]. However, it is unclear on property of adsorption of C-S-H gels on K^+ and Na^+ ions. If K^+ and Na^+ ions are chemically absorbed by C-S-H gels, they will not cause further alkali-silica reaction. Physically absorbed K^+ and Na^+ ions may be desorbed into pore solutions when concentrations of K^+ and Na^+ ions in pore solutions are lower than certain values. Shehata et al. [6] demonstrated that approximately 90% of total alkali content of the binders composed of Portland cement and 25% fly ashes or 5% silica fume may be leached into distilled water. These released K^+ and Na^+ ions may continue to bring about alkali-silica reaction. Therefore, the long term effectiveness of fly ashes on controlling ASR is uncertain although Thomas et al. [7] reported that concrete incorporated with 25% fly ash of Nant-y-Moch dam cast with reactive greywacke-argillite aggregates remained in excellent condition after 50 years in service.

In this paper, release of K^+ and Na^+ ions in cement pastes contained fly ash was investigated. It is expected that the obtained results may be helpful to understand the long-term effect of fly ashes on preventing alkali-silica reaction.

2 MATERIALS AND METHODS

2.1 Materials

Portland cement from Jiangnan-Onado Cement Limited Company in Nanjing, China was used. Class F fly ash was supplied by Huaneng Power Station in Nanjing, China. Their chemical compositions are listed in Table 1. Alkali content of cement and fly ash is 0.51% and 1.10% Na_2Oeq, respectively.

2.2 Preparation and examination of cement pastes

Cement pastes incorporated 0%, 20%, 25% and 50% fly ashes as replacements of cement were cast at a W/B ratio of 0.30. Cement pastes were sealed by a thin plastic film after casting and cured at 20 ± 2^oC.

The cement pastes were crushed and ground into powders with a particle size less than 0.080mm after cured for 90 days. The content of free water in the cement pastes was determined by measuring loss of the cement pastes dried at 105^oC. The content of the conbined water in the cement pastes was determined by measuring loss of the dried cement pastes heated at 950^oC for half an hour. The pore solutions in the cement pastes were squeezed out by a high-pressure device at 900MPa at different curing ages. FP650 flame photometer was used to examine the concentrations of K^+ and Na^+ ions in the pore solutions.

The powders in less than 0.080mm of the cement pastes were dried at 105^{o}C, and then 2.00g of dried powders of the cement pastes were immersed in 10ml of still de-ionized water at 20^{o}C. The content of Na^+ and K^+ ions in the de-ionized water was measured with FP650 flame photometer.

3. RESULTS

3.1 Effect of fly ash on concentrations of K^+ and Na^+ ions in pore solutions

Concentrations of K^+ and Na^+ ions in the pore solutions of the cement pastes are shown in Fig. 1. Content of K^+ ions increased during first 7-14 days and then decreased gradually. Content of Na^+ ions increased with increasing curing ages before 7 days, then decreased during 7-14 days and tended to be constant after 14 days. Incorporation of fly ashes may decrease the concentration of K^+ and Na^+ ions in pore solutions of cement pastes. At 90 days, the concentrations of K^+ and Na^+ ions for Portland cement pastes were 413 mmol/l and 130 mmol/l, respectively, while they were 121 mmol/l and 88 mmol/l respectively for the cement pastes with 50% fly ash. Accordingly, the content of K^+ and Na^+ ions in pore solution in the cement paste containing 50% fly ash decreased by 71% and 32%, respectively.

3.2 Release of Na^+ and K^+ ions in cement pastes in de-ionized water

Fig. 2 shows the concentrations of K^+ and Na^+ ions in 20^{o}C de-ionized water released by the dry powder samples of cement pastes cured at 20^{o}C for 90 days. According to the concentrations of K^+ and Na^+ ions as shown in Fig. 2, the contents of K^+ and Na^+ ions released by cement pastes could be calculated and were shown in Fig. 3. K^+ and Na^+ ions in the cement pastes entered rapidly into the still de-ionized water during the first 120 minutes, and then they were released by the cement pastes at a relatively slow rate. A balance between release and absorption of K^+ and Na^+ ions by the cement pastes was reached at about 720 minutes. The concentrations of K^+ ions in equilibrium were 14.6, 12.6 and 8.6 mmol/l and that of Na^+ ions in equilibrium were 3.6, 4.5 and 5.7 mmol/l in the water soaked powder samples of cement pastes containing 0%, 20% and 50% of fly ashes, respectively. The relationship between the content (Y) of K^+ or Na^+ ions released by cement pastes in de-ionized water and soaking time (X) may be described by an exponential function as presented by Fig. 4. The relative coefficient ranges from 0.8663 to 0.9738. With increasing incorporation of fly ash in cement paste, the content of K^+ ions released by cement pastes soaked in de-ionized water decreased, whereas the content of Na^+ ions released increased. This may be partially attributed to higher content of Na_2O (0.39%) in fly ash in comparison to that (0.09%) in the Portland cement (Table 1).

The evaporable water contents in the cement pastes incorporated 0%, 20%, 35% and 50% fly ashes and cured for 90 days were 12.1%, 12.9%, 13.4% and 14.5%, respectively. Based on the evaporable water contents and the concentrations of K^+ and Na^+ ions in the pore solutions of the cement pastes cured for 90 days (Fig. 1), the contents of K^+ and Na^+ ions released by the pore solutions of the cement pastes cured for 90 days could be calculated. The results are shown in Fig. 5. The total contents of K^+ ions and Na^+ ions released by drying powders of the cement pastes in de-ionized water were higher than that from the pore solutions. This implies that some K^+ and Na^+ ions in the cement pastes cured for days may not be squeezed out by 900MPa pressure.

Table 2 shows the acid-soluble and available alkali content in the mixtures of Portland cement and fly ashes, combined water content in the dired cement pastes cured at 20°C for 90 days, content of acid-soluble alkali in powders of the dried cement pastes after 90 days immersion in 20°C de-ionized water (ratio of water to powder was 100:1), corrected content of acid-soluble alkali in the dried cement pastes soaked in de-ionized water for 90 days by subtracting combined water, and alkali released into de-ionized water from the powders of the dried cement pastes. The acid-soluble alkali content in the mixtures of Portland cement and fly ashes was calculated according to data in Table 1. The available alkali content in the mixtures of Portland cement and fly ashes was calculated by considering that 100% and 15% of the acid-soluble alkali in Portland cements and fly ashes were available, respectively [8]. Researed alkali content by the dried cement pastes cured in 20 °C for 90 days and soaked in 20°C de-ionized water for 90 days (ratio of water to dry powders=100) was calculted by subtracting the content of acid-soluble alkali in the mixtures of Portland cement and fly ashes from Cac. Fig. 6 shows the proportion of released available alkali in powders of the cement pastes cured at 20°C for 90 days and soaked in 20°C de-ionized water for 90 days (ratio of water to dry powders=100). Released alkali contents based on available alkalies are 74%, 76%, 70% and 63% for the cement pastes at 90 days contained with 0%, 20%, 35% and 50% of fly ashes, respectively. No significant effect of fly ashes on retaining of available alkalies in solids of cement pastes was observed.

4. DISCUSSION

Leaching test show that 74%, 76%, 70% and 63% of available alkalis in the cement pastes contained with 0%, 20%, 35% and 50% fly ashes by weight at age 90 days were released into de-ionized water. There is no significant effect of the amount of fly ashes on proportion of released available alkalies in cement pastes. These released K^+ or Na^+ ions in de-ionized water were not chemically absorbed or bonded. They may either exist in bulk pore solutions or be physically adsorbed by hydrates. Therefore, majority of available alkalies existed in bulk pore solutions or adsorbed physically by hydrates in cement pastes may take part in alkali-aggregate reaction regardless the amount of incorporated fly ashes. Fig. 8

shows long-term effectiveness of fly ashes on inhibiting expansion of ASTM C1260 mortar bars prepared with reactive perlite aggregates and cured in 1 mol/l or 2 mol/l NaOH solutions at 80^oC. After cured in 1 mol/l NaOH solutions for 150 days or in 2 mol/l NaOH solution for 60 days, the mortar bars contained with 20%, 30% or 50% fly ashes began to expand at a relatively high rate. This seems to imply that it is needed to investigate the long term performance of concrete containing reactive aggregates and fly ashes.

5. CONCLUSIONS

(1) K^+ and Na^+ ions in cement pastes entered rapidly into de-ionized water during the first 120 minutes, and then they were released by cement pastes at a relatively slow rate. An equilibrium between the release and absorption of K^+ and Na^+ ions by cement pastes was reached at approximately 720 minutes.

(2) The total contents of K^+ ions and Na^+ ions released by the drying powders of cement pastes in de-ionized water were higher than that from pore solutions, which indicated that some K^+ and Na^+ ions in cement pastes were probably not squeezed out by 900MPa pressure.

(3) Releasable alkali contents were 74%, 76%, 70% and 63% for cement pastes contained 0%, 20%, 35% and 50% of fly ashes at 90 days. No significant effect of fly ash on the retaining of available alkalies on solids of cement pastes. These releasable alkali ions may exist in bulk pore solutions or be physically absorbed by solids of cement pastes.

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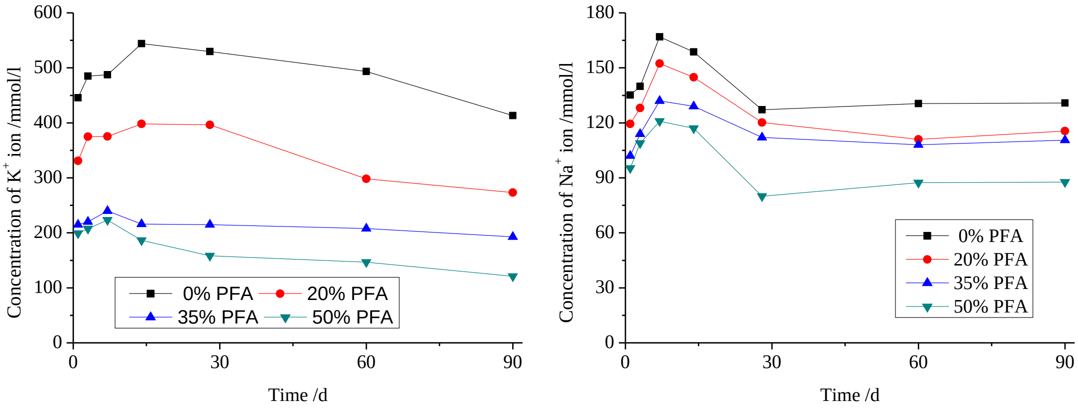
Table 1 Chemical compositions of cement and fly ash

Materials	Chemical composition /%								
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	SO_3	LOI
Cement	20.54	4.49	3.16	65.32	0.95	0.64	0.09	2.29	2.46
Fly ash	50.91	25.83	10.11	4.21	1.45	1.08	0.39	0.52	5.17

Table 2 Alkali contents in the mixtures of Portland cement and fly ashes and the cement pastes cured for 90 days

Materials	Content of acid-soluble alkali in mixtures of Portland cement and fly ashes /%	Content of available alkali in mixtures of Portland cement and fly ashes /%	Combined water content of dried cement pastes /%	Ca /%	Cac /%	Released alkali by dried cement pastes /%
0%PFA	0.51	0.51	17.9	0.11	0.13	0.38
20%PFA	0.63	0.46	17.1	0.23	0.28	0.35
35%PFA	0.72	0.40	16.6	0.37	0.44	0.28
50%PFA	0.81	0.35	15.5	0.50	0.59	0.22

Note: (1) Ca—Content of acid-soluble alkali of the dried cement pastes soaked in de-ionized water for 90 days /%；(2) Cac—Corrected Content of acid-soluble alkali of the dried cement pastes soaked in de-ionized water for 90 days by subtracting the combined water /%.



(a) K^+ ion (b) Na^+ ion

Figure 1: Effect of fly ash on the concentrations of K^+ and Na^+ ions in pore solutions of cement pastes

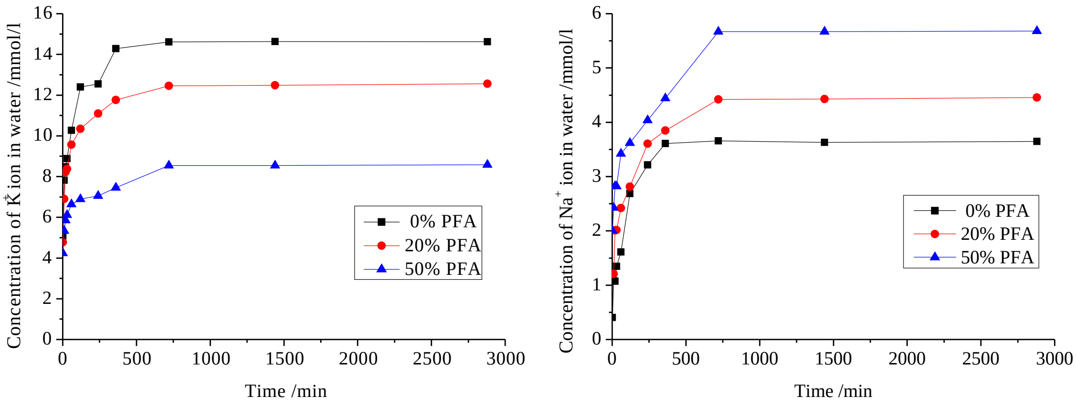
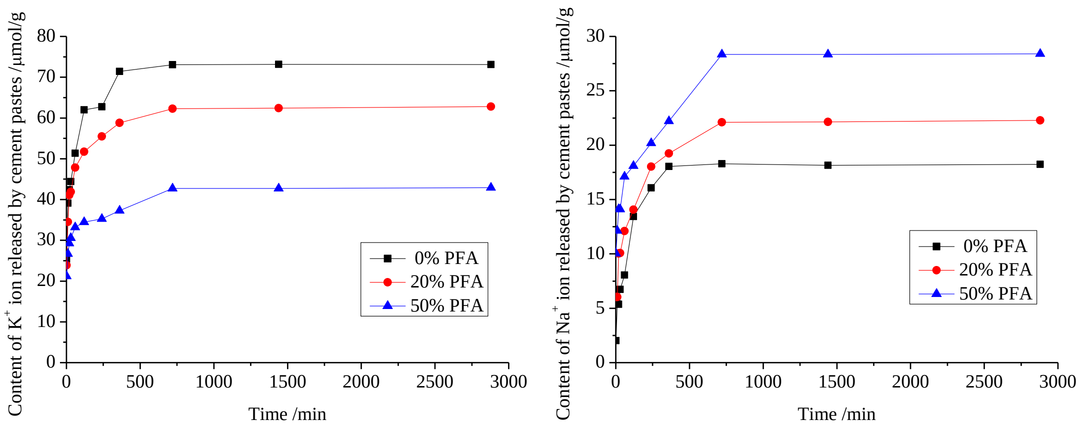
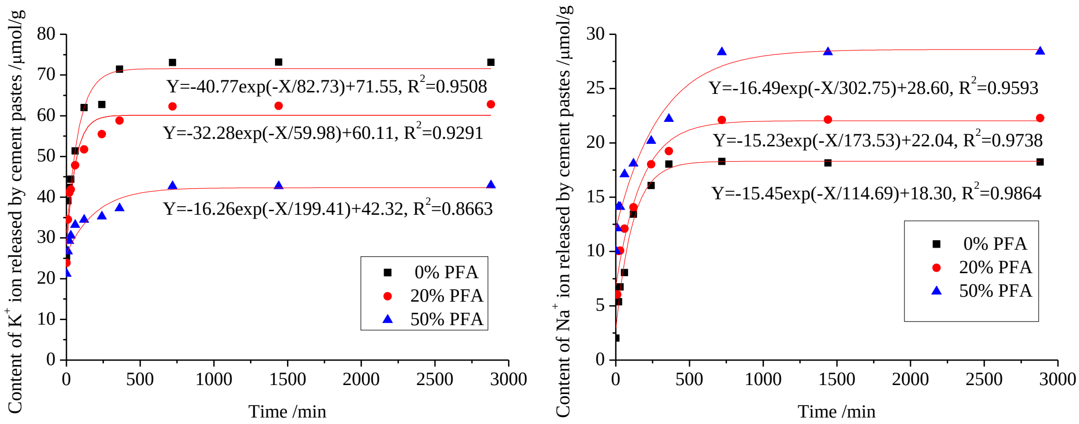


Figure 2: Concentrations of K^+ and Na^+ ions in de-ionized water soaked with dry powders of cement pastes cured at 20°C for 90 days (ratio of powder to water was 5:1)



(a) K^+ (b) Na^+

Figure 3: Contents of K^+ and Na^+ ions released by dry powders of cement pastes cured at 20°C for 90 days and immersed in 20°C de-ionized water (ratio of powder to water was 5:1)



(a) K^+ (b) Na^+

Figure 4: Relationship between the contents of K^+ or Na^+ ions released by the dry powders of cement pastes cured at 20°C for 90 days and soaking time in 20°C de-ionized water (ratio of powder to water was 5:1)

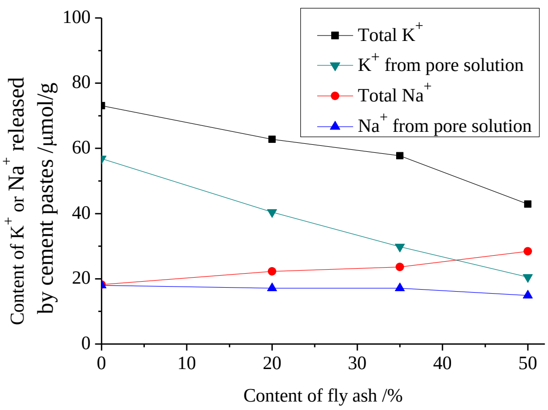


Figure 5: Contents of K^+ and Na^+ ions released by dry powders and derived from pore solutions of cement pastes cured for 90 days and soaked in 20°C de-ionized water for 3 days

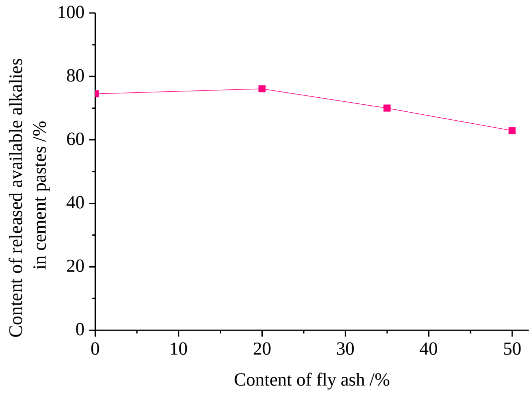
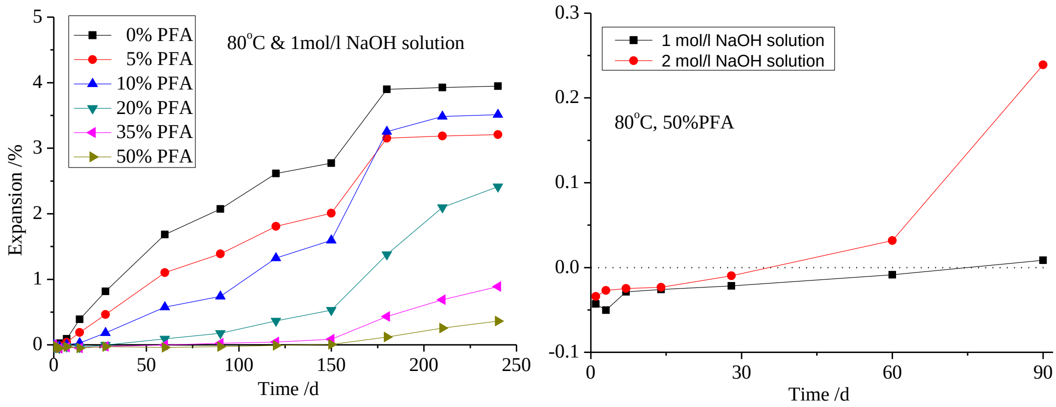


Figure 6: Proportion of released available alkalies in the powders of cement pastes cured at 20°C for 90 days and soaked in 20°C de-ionized water for 90 days (ratio of water to powder was 100:1)



(a) Cured in 1 mol/l NaOH solution (b) Cured in 1mol/l and 2 mol/l NaOH solutions

Figure 7: Expansion of accelerated mortar bars prepared with reactive perlite aggregates cured in 1 mol/l or 2 mol/l NaOH solutions