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Effect of modified zeolite on the expansion of alkaline silica reaction

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Abstract

Effect of modified zeolite (MZ) on the ASR expansion was analyzed, and comparison between MZ and other mineral admixtures such as fly ash and ground blast furnace slag was made according to ASTM C441. It is shown that the modified zeolite derived from immersion of natural zeolite(NZ) in 2 N NH_4Cl solution might decrease the concentration of soluble alkalis in pore solution more effectively, as the alkali ions could be exchanged by NH_4^+ existed in MZ with formation of $NH_3 \cdot H_2O$, as a result, the expansion due to alkali-silica reaction (ASR) was controlled consequently. In ASTM C441 test, the 14-day expansion of the specimen incorporating 5% of MZ was less than 0.1%, while the percentage of the fly ash and blast furnace slag with the same efficiency was about 25% and 40%, respectively. Physical properties of cement incorporating 5% of MZ, such as normal consistency, setting time, bending and compressive strength also met the requirement of the Chinese national standard.

Keywords: Modified zeolite (MZ); Soluble alkaline ASR

1. Introduction

Natural zeolite is a porous aluminum silicate with Si–O and Al–O bond tetrahedron as building unit [1]. As the Si^{4+} could be replaced by Al^{3+}, the tetrahedron structure is negatively charged and cations such as K^+,Na^+ could be absorbed into the tetrahedron. As a result, the natural zeolite always contains high alkaline percentage, with Na_2O_{eq} percentage of over 3% [2]. However, addition of natural zeolite in concrete could inhibit the expansion due to alkali-silica reaction (ASR) as the alkaline ions existed in concrete pore solution could yet be absorbed into the unsaturated zeolite structure, and the alkalinity of the pore solution then decreased [3]. However, the cation exchange capacity of natural zeolite is limited and the addition of natural zeolite should be no less than 20% for the effective inhibition of ASR expansion [4]; otherwise, the small dosage of natural zeolite could even enhance the expansion of alkaline silica reaction [5].

On the other hand, the natural zeolite possessed great surface area and water absorption ability, the zeolite incorporated concrete usually need more water or superplasticizer to maintain slump, and the early strength of concrete might be decreased when the zeolite percentage increases. The problems could be solved by modification of natural zeolite, through which the cation exchange of the modified product was greatly increased, and the dosage of modified zeolite (MZ) was lessened with the same effectiveness of ASR inhibition ability.

Many types of modification were available to get MZ for different purpose, such as the H^+ type zeolite, Cu^{2+} type zeolite, Na^+ type zeolite, etc. For the inhibition of ASR, the function of zeolite is to absorb K^+,Na^+ existed in pore solution and decrease soluble alkaline concentration, then NH_4 type modified zeolite is a good choice. When added into concrete, the NH_4 type zeolite might react with the ROH in concrete pore solution and decrease the content of OH^- by forming $NH_3 \cdot H_2O$, while decrease the concen-

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Table 1
Chemical composition of cement and admixtures

Materials	Chemical composition (w) (%)									Other
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	Na_2O	LOI	
Cement 1	20.36	5.04	3.70	62.04	2.85	1.75	0.62	0.13	2.67	Na_2Oe=0.57%
Cement 2	20.34	5.06	2.66	60.97	2.44	3.02	1.03	0.15	1.71	Na_2Oe=0.83%
Fly ash	45.93	24.35	9.48	6.15	2.18	–	0.91	0.41	9.61	Surface area 600 m^2/kg
Blast furnace slag	31.06	12.88	2.39	39.75	7.66	–	0.27	0.43	1.25	Surface area 600 m^2/kg
Naturas zeolite	68.42	11.78	1.61	3.12	1.12	–	2.16	0.62	9.49	NH_4^+ exchange capacity 1450 mmol/kg

tration of K^+,Na^+ by cation exchange. In this way, the expansion of ASR was inhibited with small dosage of modified zeolite, with no sacrifice of workability and early strength.

2. Experimental

2.1. Material

Natural zeolite, PO 42.5 cement with two alkaline content, and mineral powder such as slag powder, fly ash were used. High alkaline content cement (cement 2, Na_2O%=0.83%) was used for strength experiment and low alkaline cement (cement 1, Na_2O%=0.57%) was used in ASTM C441 to determine the effectiveness of the mineral powders in suppressing ASR expansion. Additional NaOH was added to increased the Na_2O content of binder to 1.0±0.05% in the ASTM C441 test. The chemical composition of the cements and admixtures was shown in Table 1.

2.2. Test details

2.2.1. Modification of natural zeolite

The natural zeolite powder was immersed in 2 N NH_4Cl solution for 4 h to exchange the K^+ and Na^+ with NH_4^+, then the product was washed with water to remove the impurities and the exchanged cations, the product was then dried and ground, and sealed for use.

2.2.2. Absorption properties of natural zeolite and modified zeolite

The powder of natural zeolite and modified zeolite was put into the NaOH and KOH solution of different concentration, the concentrations of the solution were periodically measured, and the absorption properties of zeolite was determined by the concentration change of the solution. The concentration of the immersing alkaline solution was simulated according to the pore solution of the mortar for strength test, calculated by the alkaline content and w/c ratio. According to the china national standard GB12958-1999, the cement and water used for the mortar preparation was 450 g and 225 ml, respectively, as the Na_2O content of the low and high alkaline cement was 0.57% and 0.83%, the alkaline concentration of the corresponding pore solution was about 0.30 and 0.42 N, provided that the soluble alkaline was about 80%. Alkaline solution of the two concentration was mixed with NaOH and KOH as reagent, while 45 g zeolite (10% of cement) was put into 225-ml alkaline solution to test for the change of alkaline concentration.

2.2.3. Effect of modified zeolite on cement properties

The properties of the ordinary Portland cement and the modified zeolite incorporated cement were examined, including strength, setting time and normal consistency.

2.2.4. Effect of the mineral powders on the suppression of ASR induced expansion

Many methods were employed to examine the effectiveness of mineral admixture on the expansion due to alkali-silica reaction, such as ASTM C1260 [6] ASTM C441 [7], etc., the former cured the specimens in 1 N NaOH solution at 80 °C to accelerate the alkali-silica reaction by increasing alkalinity and temperature, the later substitute concrete aggregate with quartz glass, and the acceleration of reaction was realized by the high reactivity of the quartz glass. As the inhibition of ASR expansion by modified zeolite was realized mainly by the absorption of soluble alkaline, the ASTM 1260 method was not suitable to evaluate the effect of modified zeolite on ASR expansion, for the small dosage of modified zeolite was not enough to reduce the alkalinity of concrete specimens immersed in 1 N NaOH solution, even the saturated exchange point was reached. The late method, ASTM C441, however, was similar to the field

Table 2
The size and percentage of quartz glass specified in ASTM C441

Diameter	0.15–0.3 mm	0.3–0.6 mm	0.6–1.18 mm	1.18–2.36 mm	2.36–4.75 mm	Total
Percentage	15%	25%	25%	25%	10%	100%
Mass	135	225	225	225	90	900

Table 3
Mix proportion of the specimens according to ASTM C441[a]

Specimen	Cement (g)	Admixture (g)	Quartz sand (g)	Water (ml)
KB	400	–	900	188
SL1	280	120	900	188
SL2	200	200	900	188
FA1	280	120	900	188
FA2	240	140	900	188
MZ1	380	20	900	188
MZ2	340	60	900	188
MZ3	300	100	900	188

[a] KB is the controlled specimen, and SL1—slag content 30%, SL2—slag 50%, FA1—fly ash 30%, FA2—fly ash 40%, MZ1—modified zeolite 5%, MZ2—modified zeolite 15%, MZ3—modified zeolite 25%. In the preparation of the specimens, NaOH should be added in the mix to adjust the Na_2O content 1.0±0.05% (w) of the binder and superplasticizer was added in appropriate amount in the MZ specimens to ensure their workability.

condition and the method was suitable for the examination here.

ASTM C441 was employed in this paper to examine the effect of mineral powder on ASR induced expansion. The size and percentage of the quartz glass used was shown in Table 2; the cement and mineral powder proportion was shown in Table 3.

3. Results and discussion

3.1. Concentration change of NaOH and KOH solution with addition of zeolite

The concentration change of NaOH and KOH solution after zeolite absorption was shown in Figs. 1 and 2. The immersing alkali solution of Fig. 1 was 0.30 N NaOH and KOH, and the alkaline solution in Fig. 2 was 0.43 N NaOH and KOH.

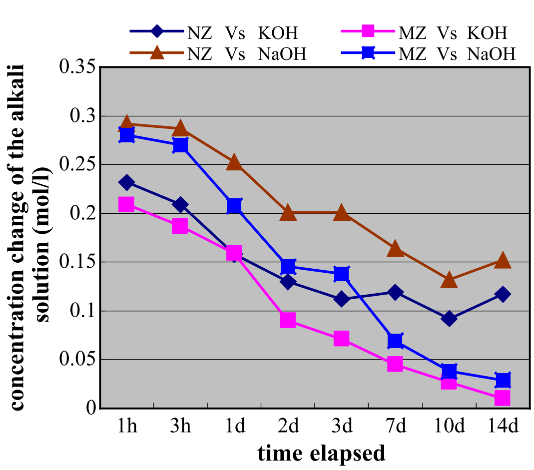

Fig. 1. Concentration change of the alkali solution in the process of zeolite absorption (for cement 1).

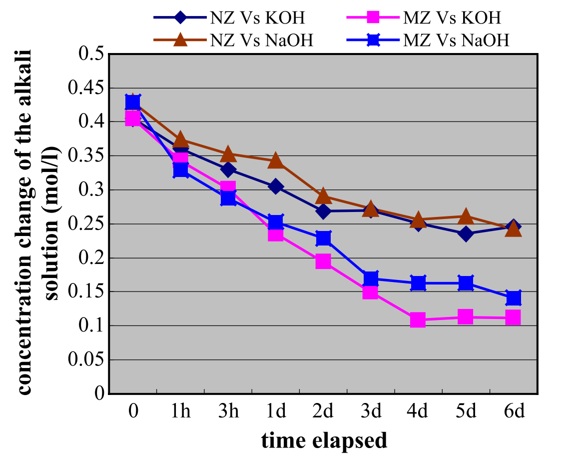

Fig. 2. Concentration change of the alkali solution in the process of zeolite absorption (for cement 2).

It is seen from Fig. 1 that both natural and modified zeolite were able to absorb the K^+ and Na^+ in the solution, but the speed and exchange capacity were different. At 3 h, the KOH and NaOH exchange capacity of modified zeolite was 15.55/45 g and 9.08 mmol/45 g, respectively, 55% and 91.12% higher than that of the natural zeolite; after 3 days of absorption, the absorption of KOH and NaOH by modified zeolite were 41.16 mmol/45 g and 39.71 mmol/45 g, 29.88% and 59.09% higher than that of the natural zeolite.

With the ongoing of the absorption, the alkalinity of the solution mixed with modified zeolite decreased on until to nil, while the natural zeolite decreased the alkalinity of NaOH to 0.132 N and KOH to 0.095 N, then the concentration of the solution increased a little, showing the saturation of the absorption. At this point, the exchange capacity of modified zeolite was 63.74/45 g for KOH and 49.36 mmol/45 g for NaOH, 53.1% and 51.2% higher than that of natural zeolite. The effective absorption of the alkaline ions, as well as the neutralization of the hydroxide ion considerably decreased the content of soluble alkaline in the pore solution, and the alkali-aggregate reaction was thus effectively inhibited.

It is also shown from Fig. 2 that the speed of alkaline absorption was increased with concentration increase of the immersing solution. The absorption capacity of KOH by modified zeolite in 1 h was 15.55 mmol, about the amount of the 3 h absorption in scarce solution (0.30 N), and the 1 h absorption of NaOH was 25.00 mmol, about the amount of the 24-h absorption in scarce solution. The exchange get to equilibrium after 5 days of absorption, during which the exchange capacity of KOH and NaOH was 68.6 and 62.56 mmol/45 g, 72.4% and 58.5% higher than natural zeolite.

It is known from the analysis that the speed of ion exchange increased with the increase of ion concentration of the immersing solution, and the absorption speed and the maximum exchange capacity of modified zeolite was 30–

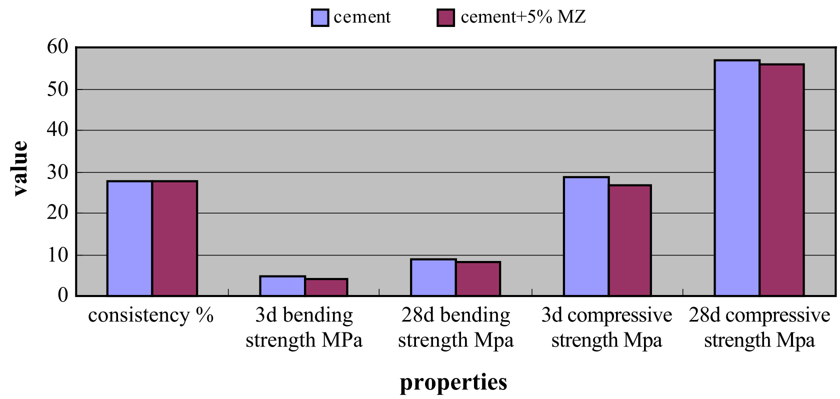

Fig. 3. Effect of modified zeolite (GNZ) on cement properties.

50% greater than that of natural zeolite, while the absorption capacity of K^+ was bigger than Na^+.

3.2. Effect of modified zeolite on cement properties

The physical properties of high alkaline cement and the cement with addition of 5% modified zeolite were shown in Fig. 3.

It is seen from Fig. 3 that the normal consistency of the cement paste with 5% of MZ was similar to the controlled specimens, and the 3-day compressive strength and flexural strength decrease about 5–7%, while 28-day strength was commensurate as well, and all the indexes meet the requirement of the Chinese national standard GB12958-1999.

3.3. Inhibition effect of zeolite and other mineral admixtures on ASR expansion

The inhibition effect of zeolite and other mineral powders on the ASR expansion was shown in Figs. 4 and 5.

It is seen from Figs. 4 and 5 that the ASR expansion might be effectively inhibited by the addition of different mineral powders, and the best result was achieved when modified zeolite was added. In Fig. 4, the 14-day expansion of the mortar bar was decreased to 0.071% when cement was replacement with 5% of modified zeolite, about 25% of the expansion of the controlled specimens, and the ratio of expansion decreased further to 0.023% and 0.021% when the percentage of modified zeolite increased to 15% and 25%, respectively.

The effect of different mineral powders on the ASR expansion was shown in Fig. 5. It is shown that the expansion ratio of the specimens with 30% and 50% of slag was to 0.085% and 0.044%, while the addition of 30% and 40% of fly ash decreased the ratio to 0.068% and 0.022%, respectively. The effect of fly ash was better than slag, partly because it decreased the alkalinity of the pore solution more effectively [8].

Comparison of the two figures showed that the effect of 5% of MZ was better than 30% of slag, but less than 30% of fly ash and 50% of slag, or about the same efficiency of 25% of fly ash or 40% of slag. It is imaginable that, with the increase of MZ addition, the ratio of expansion would be further decreased, but the bigger dosage of modified zeolite would do harm to the early strength of mortar and concrete, and workability of fresh concrete would also be affected or the dosage of superplasticizer would be increased accompanied by the increase of cost. In other words, the application of 5–10% of modified zeolite was a better choice in the area where the non-reactive aggregate was not available.

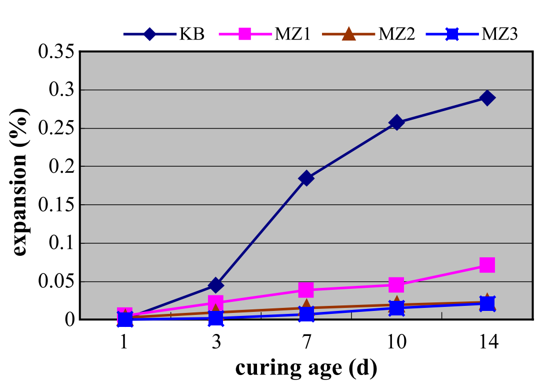

Fig. 4. Effect of modified zeolite on ASR expansion.

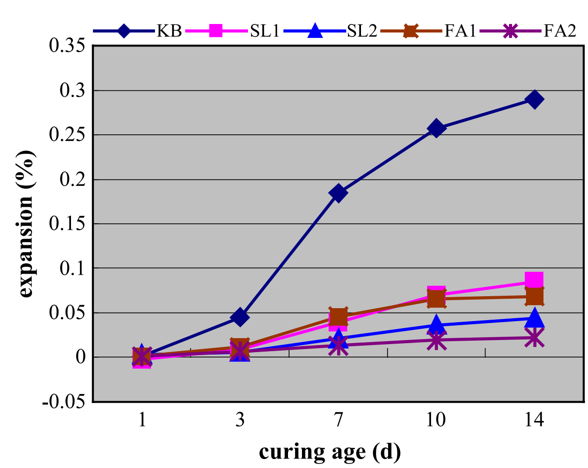

Fig. 5. Effect of fly ash and slag on ASR expansion.

4. Conclusion

Through the modification of natural zeolite, the exchange capacity of alkaline ions was greatly increased and the speed of absorption increased with the increase of the immersing alkaline solution concentration. In the solution of 0.43 N NaOH and 0.40 N KOH, the maximum absorption capacity of modified zeolite was 68.60 mmol/45 g and 62.56 mmol/45 g, 50%–70% higher than that of natural zeolite. In the low concentration solution of KOH and NaOH, the alkaline ions were fully absorbed.

The substitution of cement with 5% of modified zeolite might decrease the ratio of expansion to less than 25% of the controlled specimens, about the same efficiency of 25% fly ash or 40% of slag. As the amount of modified zeolite was small, the strength and workability of the mortar and concrete was not changed as well.

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