# EFFECT AND MECHANISM OF NATURAL ZEOLITE FOR PREVENTING EXPANSION DUE TO AAR

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The expansion of the mortar bar with zeolite cement (ZC) and hard glass is 0.004%(28 days) and -0.003% (90 days), the portland cement for dam(0.62% total alkali) is 0.599% (90 days) and the mortar bars with ZC and non-reactive sand is -0.003%(28 days) and -0.004%(90 days) respectively. It is sure that there is no damage from AAR though concrete is made of ZC with reactive aggregate.

## INTRODUCTION

The annual output of cement in China amounts to more than 200,000 thousand tons, and two-third of the output is made by vertical kiln. One-third of the cement output by vertical kiln is blended with natural zeolite(1). There exists a great amount of reactive $SiO_2$ and $Al_2O_3$ in natural zeolite, so that the density and the strength of the concrete blended with natural zeolite increases much with the age owing to pozzolanic reaction(2). On one side, the natural zeolite as the blending material of cement concrete is expected to prevent the expansion due to AAR by the ion absorption and the ion exchange. On another side, natural zeolite with high amount of $Na_2O$ and $K_2O$ might increase the expansion due to AAR. In this research zeolite cement (ZC) is used and the expansion due to AAR is investigated by the mortar-bar testing method.

## RAW MATERIALS

ZC with a ratio of natural zeolite, cement clinker and gypsum of about 30%:65%:5% is used. The content of alkali in ZC is about 1.42%. A dam cement(DC) is used as the control cement. Its alkali content is about 0.62%. In this research the content of alkali in part of ZC was raised to about 1.82%by adding NaOH.

The principal mineral in the zeolite is clinoptilolite which makes up about 60% of the material.

Quartz sand was used as non-reactive aggregate in this research.

Hard glass and andesite (Sc=747mmol/L, Rc=194mmol/L) were used in this research. The two kinds of aggregates are judged as being harmful to concrete according to ASTM C 289 .

## EXPEREMENTS

Tests comparing the DC and ZC, hard glass and quartz sand were first made as shown in Table 1.

TABLE 1- Tests comparing the cement for dam and ZC, hard glass and quartz sand

| Number | Cement Type | Alkali Content | Aggregate Type and its content |
|---|---|---|---|
| Control | DC | 0.62 | Hard Glass 100% |
| 1 | ZC | 1.42 | Hard Glass 100% |
| 2 | ZC | 1.82 | Hard Glass 100% |
| 3 | ZC | 1.42 | Quartz Sand 100% |
| 4 | ZC | 1.82 | Quartz Sand 100% |

Experimental Methods The experimental methods in China for hydraulic concrete are used(3). The ratio for mortar by mass is: Cement:Sand=1:2.25, and the water mass is based on flow of about 105-120 mm. All the materials used in the tests are kept in a room with a constant temperature of $20^{+}1.7^{0}C$ for $24^{+}2$ hours, Freshly-mixed mortar was cast in three 25x25x285 mm moulds that were stored in a controlled room. The specimens were demoulded after curing for 2-3 days, and their lengths measured, then the specimens are cured in box at a temperature about $38^{0}C$ with a relative humidity greater than 95%. Before the next measurement, the specimens were moved to a room with the constant temperature about $20^{0}C$ for $24^{+}2$ hours. The readings were taken again and the change in the lengths computed.

## RESULTS AND DISCUSSION

The Test Results for the DC AND ZC-(1) Tests comparing the cement for dam and ZC. The test results are shown in Fig.1. The alkali contents were about 0.62% in the DC, 1.42% and 1.82% in ZC. At one year, the expansion rate of the mortar bar made from DC and fine hard glass was about 0.106%, but the corresponding values of the mortar bar made from ZC and hard glass were only about 0.004% and 0.002%, which shows that the cement (ZC) blended with 30% natural zeolite is effective in preventing the expansion due to AAR; (2) Tests comparing reactive aggregate and non-reactive aggregate for ZC The results shown in Fig.2 indicate that the expansion of the mortar bar made from ZC and reactive aggregate (No.1 and 2) is about 0.004% and -0.003% at the age of 13 weeks, as for the mortar bar made from ZC and non-reactive aggregate (No.3 and 4) is -0.006% and -0.004% at this age.

According to the standard testing method of hydraulic engineering concrete in China(4), there are two standard evaluating methods:

(a) The expansion rate of the mortar bar must be less than 0.02% at 14 days.

(b) The ratio of the difference in the expansion between the mortar bar being tested and the control bar must be greater than 75% at 14 days, and the expansion must not exceed 0.05% at the age of 56 days. The cement which can satisfy the two requirements mentioned above can be used with reactive aggregate without exhibiting harmful AAR.

From the results obtained here, the expansion of the control mortar bar at the age of 14 days was measured as:

Er=0.0935%.

The expansion of the comparing mortar bar at the age of 14 days is:

Et(-1)=0.009% ┐
├ (replaced by the results at the age of 28 days)
Et(-2)=0.002% ┘

Et(-1) for the alkali content of ZC is 1.42%;
Et(-2) for the alkali content of ZC is 1.82%

Both results are less than 0.02% and meet the first requirement of 366-80. For the second requirement, the ratio is:

Rl=(Er-Et)/Er
Rl(-1)=90%>75%
Rl(-2)=98%>75%

And the expansions of the mortar bars at the age of 56 days are less than 0.05% for Et(-1) and Et(-2).

The computed results mentioned above show that the standard evaluating requirements can be satisfied for ZC, ZC can be used to the concrete containing reactive aggregates, and harmful AAR can then be avoided.

Mechanisms of Natural Zeolite on Preventing the Expansion due to AAR.

The reaction of silicate and sodium hydroxide (or potassium hydroxide) results in the formation of the gel of sodium silicate (or potassium silicate). The gel absorbs water and swells. The expansion of the gel exerts pressure in the concrete and results in the failure of concrete.

$$-Si-OH + Na^{+} + OH^{-} \longrightarrow \underbrace{-Si-O-Na^{+}}_{gel} + H_2O$$

at high concentration of $OH^-$

$$-Si-O-Si- + 2NaOH \longrightarrow \underbrace{-Si-O-Na^{+} + Na^{+}O^{-}-Si}_{gel} + H_2O$$

The concentration of sodium and potassium ions in solution in the fine pores of hardened cement paste can be lowered by the ion exchange of natural zeolite, so that the formation of Si-ONa and AAR can be eliminated.

In the experiments, 0.8 g of sodium hydroxide was added into 20 mL of pure water, followed by 15g of natural zeolite. After mixing completely, filtering and washing, the pH value of the solution was 7. The calcium and potassium ions in the natural zeolite lattice are exchanged for sodium ions. The natural zeolite after the ion exchange is called the "exchanged zeolite". The primary natural zeolite and the exchanged zeolite (amount 100 mg) were added to 20 mL of $NH_4Cl$ solution with a consistency of 1N, boiled for 2 hrs, then filtered and washed to free the solution of chlorine ions. After this process, the solution was diluted to a volume of 100 mL, and the contents of calcium , sodium and the potassium oxides determined.

The sodium oxide content in the exchanged zeolite was fount to increase, but calcium and potassium oxides decreased. The results indicate ions exchange of calcium and potassium for sodium. After the exchange, the $Na^+$ ions exchanging for other ions in natural zeolite in mg equivalent of $Na_2O$ was (2.54-1.96)*100/31=1.87. The content of the $Ca^{2+}$ ions exchanged in mg equivalent of CaO is (2.17-1.74)*100/28=1.53, and $K^+$ ions exchanged in mg equivalent of $K_2O$ was (2.33-2.26)*100/47=0.15. The sum of the mg equivalent of $K_2O$ and CaO exchange for $Na_2O$ is 1.53x1.107+0.15x0.659=1.79, similar to that of $Na_2O$ (1.87). It may be concluded that the action of NaOH on natural zeolite results in decreasing the NaOH, which is caused by the ion exchange.

Further research was conducted on ZC blended with 30% natural zeolite. At W/C of 0.4, the initial alkali concentration was controlled to 3.5, 8.7, 20.0, 26.0 and 34.0 mg/mL by adding NaOH, After adding natural zeolite to the solutions the consistencies of alkali were determined. In order to simplify the experiment, the water solutions with the same initial consistencies of alkali before adding natural zeolite were used. The results are presented in Table 3. It shows that the concentrations of alkali are conspicuously decreased by adding natural zeolite.

TABLE 3- The concentration of alkalis in water before and after adding natural zeolite

| No. | Water (mL) | Amount of Zeolite Added (g) | Concentration of Alkali in Water before Adding Zeolite[$Na_2O$(mg/mL)] | Concentration of Alkali in Water after Adding Zeolite[$Na_2O$(mg/mL)] | Balance $Na_2O$(%) |
|---|---|---|---|---|---|
| 5 | 40 | 30 | 3.5 | 0.6 | 17.1 |
| 6 | 40 | 30 | 8.7 | 1.2 | 13.8 |
| 7 | 40 | 30 | 20.0 | 4.0 | 20.0 |
| 8 | 40 | 30 | 26.0 | 6.5 | 25.0 |
| 9 | 40 | 30 | 34.0 | 11.0 | 32.4 |

Note: W/(C+Z)=0.4, Water mass is 40 mL, C+Z=100g, Z=30g.

We made tests and observations to ascertain the results above. The materials and mass ratios of the concrete tests are shown in table 4. Three types of concrete are made and cured in standard curing condition(20±2°C, RH.>90%)for 5 months. It was observed that the specimens made from portland cements and andesite are filled with gel of sodium silicate on the surface, but the surface of the specimens made from ZC and andesite were free from this gel(Fig.3). The results confirm that AAR can be prevented by adding zeolite to concrete.

TABLE 4-The concrete mix ratio and materials

| No | Cement type | Alkali content(%) | Blending content of zeolite | S/C | Mix ratio (by mass) C | G | Content of reactive aggregate(%) |
|---|---|---|---|---|---|---|---|
| 10 | Portland Cement | 0.8 | 0 | 0.4 | 10 | 1 | 100 |
| 11 | Portland Cement | 2.8 | 0 | 0.4 | 10 | 1 | 100 |
| 12 | ZC | 2.8 | 30 | 0.4 | 10 | 1 | 100 |

## CONCLUSIONS

1 According to the standard test method of hydraulic engineering concrete (366-80) in China, if ZC is used together with reactive aggregate applying to mortar or concrete, harmful AAR can be avoided.

2 Natural zeolite as the retarding material of AAR can eliminate the concentration of the alkali ions in the cement paste mainly owning to the ion exchange. Therefore the reaction between reactive aggregate and the alkali ions in the solution in the fine pores of cement paste is also eliminated, so the condition of Si-ONa formation is destroyed and the expansion due to AAR is retarded.

## REFERENCES

1. Wu Zhongwei and Feng Naiqian. Aug. 1989," Cement and Concrete in China-Past, Present, Future", Cement concrete No.510.

2. Feng Naiqian, Takeshi Mukai, and Kyor Ehara. June,1988,"A Study on the Effect of Zeolite when Used as Admixture of Concrete", Journal of Structural and Construction Engineering, No. 388.

3. GB 200-80 ( Standard of Cement for Dam in China)

4. GB 366-80 (Standard Testing Method of Hydraulic Engineering Concrete in China)

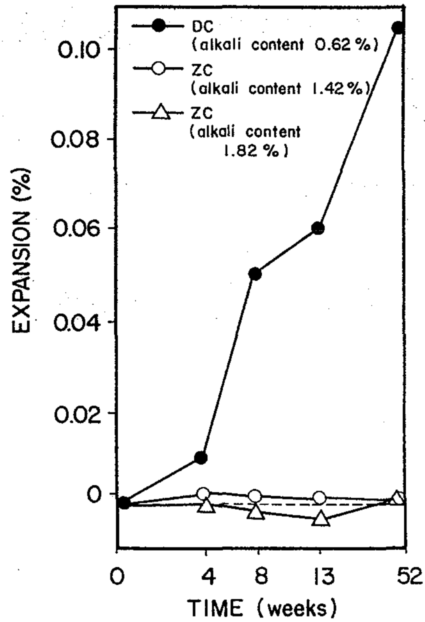



Fig.1 The effect of ZC and DC on the expansion due to AAR

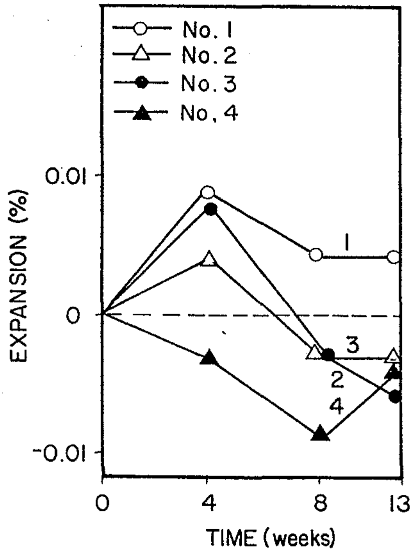
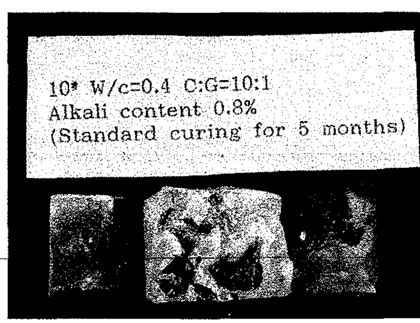
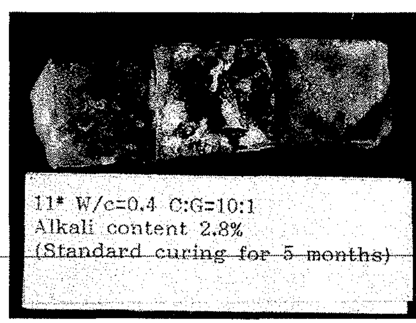



Fig.2 Comparing reactive and non-reactive aggregate in ZC cement



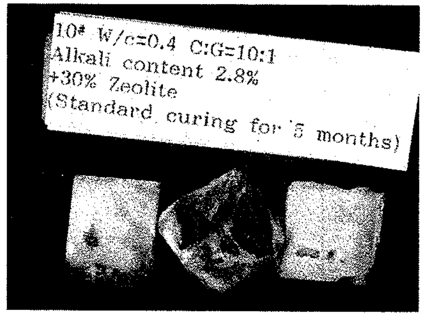



Fig.3 Photos of the concrete specimens with and without ZC