Pergamon

Cement and Concrete Research 32 (2002) 851–857

CEMENT AND CONCRETE RESEARCH

A new accelerated method for determining the potential alkali-carbonate reactivity

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Received 7 August 2000; accepted 2 December 2001

Abstract

Many kinds of carbonate aggregates with different chemical compositions, structure, and geological characteristics have systematically been investigated. This research deals with chemical components and mineral analysis, petrographic examination of the aggregates, the dynamics of alkali-carbonate reaction with different cements, alkali contents, and particle sizes. A new method for evaluating the potential alkali-carbonate reactivity has been proposed according to the results, in which the major test factors include 1.5% $Na_2O_{eq.}$ of alkali content, 1 M NaOH solution, 0.3 water-to-cement ratio, 5–10 mm particle size, and 4 weeks of test period at 80 °C. The results using this new method has also been compared with that of the performance of concrete structures in China. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Alkali-carbonate reaction; Accelerated method; Reactive aggregates; Durability of concrete

1. Introduction

Since the field deterioration of concrete structures due to alkali-carbonate reaction (ACR) was first reported in the 1950s in North America, and investigated by Swenson and Gillott [1] and Gillott [2], more research attention has been paid to this topic by many researchers [3,4]. The major contents are the mechanism and test methods of ACR as well as the field inspections. The progress of ACR study leads us to know that an ACR problem cannot be as easily inhibited as an alkali-silica reaction (ASR). The primary important issue is how to identify the reactive carbonate aggregates for the purpose of avoiding it. It seems that developing a rapid method for testing the reactivity of carbonate aggregate is essential because of the short lead time available before the construction period.

A great deal of infrastructure development has occurred in the past 20 years in China, and many limestone and dolomite aggregates have been used. Field inspections and laboratory investigations have shown that deleterious effects have been caused by ACR in different concrete structures in several provinces in China, for example, damage to piles, railway ties, airports, and bridges [5]. In all these cases, high alkali cement and reactive dolomitic limestone or dolomite aggregates were used. Research works on the mechanism of ACR and test method for detecting reactive dolomitic aggregates have continued and been enhanced in recent years because of the significant financial support by the government since 1996.

It is well known that there is no quick test method for determining the alkali reactivity of carbonate rocks. The Canadian concrete method takes a long time to perform and is not satisfactory for Chinese practical needs. Based on this view, a rapid method for ACR was proposed by us [6], which was based on improvement of the ASR autoclave method. It has been noted that this method poses some barriers for engineering management, for example, too small mortar bar size that leads to large variations in the data, and too small amount of aggregate that may not be representative of actual rocks and quarries. The present project aims at developing a rapid test method for determining the alkali reactivity of carbonate rocks with more acceptable engineering feature, and with more reliable results.

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PII: S0008-8846(01)00758-X

2. Carbonate aggregate samples

In order to obtain as many typical samples as possible, many kinds of carbonate aggregates have been collected from all over China, and the quarries have also been investigated by authors and the geologists at Nanjing University. The rocks tested come from different geological ages, for example, Sinian, Cambrian, Ordovician, Dias, Trias, etc. This covers almost all carbonate aggregates that have been reported as reactive in field concrete structures. The petrographic characteristics of samples were analyzed by microscopy, and the results are shown in Table 1.

3. Test methods

3.1. 150 °C autoclave method

This method was proposed previously by authors as a quick screening test [6]. The major factors of the procedure include test temperature of 150 °C, 5–10 mm size of aggregates, alkali solution of 10% KOH, alkali content of 1.5% $Na_2O_{eq.}$ in cement, and 6 h of test period. It is quite similar to "The Chinese Autoclave Method for ASR," but a different aggregate size was used.

3.2. New method

The accelerated mortar bar test method for ASR, involving storage of mortar bars in 1 M NaOH at 80 °C, has been used in the past 15 years. This method uses the fine aggregate grading of ASTM C-227. The results of this test have correlated well with field performance of aggregates for ASR. With reference to ACR, Shayan et al. [7] showed that these conditions were not suitable if the normal mortar bar grading of ASTM C-227 is used. It was found for reactive carbonate rocks, such as CK aggregate, that the 80 °C, 1 M NaOH conditions were more suitable for coarse aggregate, but the mix design of concrete prisms did not provide optimum expansion.

Therefore, most of the work in the present study was carried out at 80 °C. All carbonate aggregate samples were crushed and graded for testing into 5–10, 2.5–5, 1.25–2.5, and 0.8–1.25 mm. For comparison with this method, tests were also carried out at 40 °C with a similar procedure to that at 80 °C. The molding and precuring procedures were similar to the autoclave method, but different raw materials and test conditions were used. The water-to-cement ratio of 0.3 was used, and aggregate-to-cement ratio was 1:1. All specimens with size of $20 \times 20 \times 80$ mm were stored in 1 M NaOH solution. Some specimens were $40 \times 40 \times 160$ mm in size, and will be specially remarked on in this paper.

The alkali content of the low-alkali cement from Jiangnan Cement is 0.52% $Na_2O_{eq.}$. Alkali solution (KOH) was added in mixing water to make the total alkali content of cement 1.5% $Na_2O_{eq.}$. The alkali content of the high-alkali cement from Jidong Cement is 1.24% $Na_2O_{eq.}$. Alkali solution (KOH) was also added in mixing water to make the total alkali content of cement 1.5% $Na_2O_{eq.}$.

4. Results and discussion

4.1. ASR, ACR, and thermal expansion by autoclave screening test

All samples were primarily tested by the quick method (150 °C) for determining alkali-silica and and alkali-

Table 1
Carbonate rock samples investigated and their petrographic characteristics

No.	Geological age	Quarry location	Geologic characteristics
C	Leikepo Formation, Triassic	Guanyuan, Sichuan	Macromeritic dolomite
CK	Gull River Formation, Ordovician	Kingston, Canada	Argillaceous dolomitic limestone
ZK	Triassic	Yibin, Sichuan	Dolomitic limestone
QJ	Bei An Zhuang Formation, Ordovician	Upper layer in Baofu Mountain, Lin Qu	Thin layer structure, dolomitic limestone
LB	Bei An Zhuang Formation, Ordovician	Lower layer in Baofu Mountain, Lin Qu	Leonard dolomitic limestone
T1	Majiagou Formation, Ordovician	Tangshan, Hebei	Pure dolomite
T2	Ibid.	Ibid.	Leopard limestone
T3	Ibid.	Tangshan, Hebei	Leonard dolomitic limestone
T4	Ibid.	Ibid.	Dolomite with more quartz
ATJ	Wu Mi Mountain Formation, Sinian	Jixian county, Tianjin	Argillaceous dolomite
JD1	Yeli Formation, Ordovician	Jidong, Hebei	Leopard deep gray limestone
JD2	Ibid.	Ibid.	Leopard light yellow limestone
Z1	Zhangxia Formation, Cambrian	Liantai Mountain, Jinan, Shandong	Leopard oolitic limestone
Z2	Ibid.	Ibid.	Leopard argillaceous limestone
Z3	Ibid.	Ibid.	Leopard micritic limestone
JC	Wu Mi Mountain Formation, Sinian	Jixian, Tianjin	Microlitic dolomite
JH1	Hongshui Mountain Formation, Sinian	Jixian county, Tianjin	Argillaceous silt dolomite
JH2	Ibid.	Ibid.	Argillaceous microlitic dolomite
WB1	Feng Mountain Formation, Cambrian	Weifang, Shandong	Argillaceous dolomitic limestone
WB2	Ibid.	Ibid.	Argillaceous limestone

carbonate reactivities, and the results are shown in Table 2. The $20 \times 20 \times 80$-mm mortar bar size was used in this test. It is clear that samples JD1, JH1, and JH2 possess alkali-silica reactivity and that T4 may be potentially reactive. These carbonate aggregates contain larger amounts of silica components than the other aggregates, which show much microcrystalline quartz by petrographic examination. It should be noted that these rocks appear to be alkali-carbonate reactive, because the expansions of mortar bars containing these aggregates increase sharply with storage period in the ACR test. They also cause large expansions in the ASR. It can be concluded that these rocks are both alkali-silica and alkali-carbonate reactive.

Besides the above rocks, the other carbonate aggregates can be identified as being nonreactive for ASR. This means that the expansions of samples caused by ASR are negligible compared with total values. On the other hand, coarse crystalline dolomite C (non-alkali-silica and non-alkali-carbonate reactivities) or pure cement pastes or mortars show very low expansion values at high temperature even after a long treatment period. This indicates that no obvious expansion was caused by heat of hydration of cement pastes and minerals in the rocks.

Table 2
Expansion behavior of samples by autoclave method

No.	ACR expansion (%) Size (mm)	6 h	12 h	30 h	54 h	80 h	ASR test
C	5–10	0.029	0.040	0.038	0.060	0.056	
CK	5–10	0.093	0.158	0.222	0.298	0.343	0.011
LB*	5–10	0.072	0.154	0.238	0.283	0.321	0.021
LB2-1	2.5–5	0.123	0.211	0.336	0.373	0.402	
LB2-2	1.25–2.5	0.117	0.202	0.323	0.329	0.336	
LB2-3	0.8–1.25	0.199	0.293	0.326	0.319	0.324	
QJ	5–10	0.099	0.190	0.321	0.406	0.481	0.021
QJ-1	2.5–5	0.139	0.230	0.320			
QJ-2	1.25–2.5	0.137	0.242	0.305	0.302	0.311	
QJ-3	0.8–1.25	0.127	0.182	0.249	0.241	0.246	
ATJ	5–10	0.137	0.211	0.456	0.879		0.037
ZK	5–10	0.124	0.279				0.034
T1	5–10	0.048	0.127	0.227	0.299	0.331	0.015
T2	5–10	0.115	0.195	0.321	0.425	0.516	0.062
T3	5–10	0.117	0.224	0.404	0.496	0.591	0.066
T4	5–10	0.104	0.275	0.499	0.645	0.803	0.090
JD1	5–10	0.056	0.165	0.383	0.648	0.809	0.109
JD2	5–10	0.075	0.196	0.332	0.402	0.441	0.025
Z1	5–10	0.066	0.105	0.194	0.253	0.286	0.015
Z2	5–10	0.106	0.147	0.196	0.257	0.294	0.029
Z3	5–10	0.111	0.202	0.288	0.344	0.360	0.023
JC1	5–10	0.064	0.093	0.214	0.286	0.359	0.024
JH1	5–10	0.069	0.164	0.415	0.572	0.852	0.143
JH2	5–10	0.116	0.248	0.873			0.184
WB1	5–10	0.060	0.115	0.213	0.307	0.366	−0.031
WB2	5–10	0.076	0.130	0.237	0.299	0.434	

The names of samples -1, -2, and -3 represent particle sizes of 2.5–5.0, 1.25–2.5, and 0.8–1.25 mm of the same aggregate.

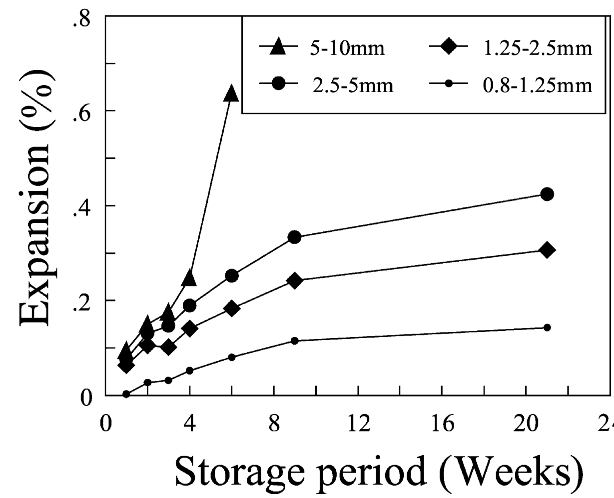

Fig. 1. The expansion curve of argillaceous dolomite from Tianjin (ATJ).

4.2. Influence of particle size on ACR expansion

High temperature, high alkali content, and use of sensitive particle size are the bases of accelerating alkali-aggregate reaction (AAR) tests. An important key factor in controlling AAR may be the size of aggregate particles as found by many authors. It is clear that most methods utilize 80 °C temperature, at which no obvious modification of the nature of AAR products takes place compared to ambient temperature or 40 °C. Therefore, the present research aims at a temperature of 80 °C as a standard, and studies the influences of the other key factors and the expansion dynamics of various carbonate aggregates.

Various potentially reactive aggregates (ACR) were tested with 1.5% $Na_2O_{eq.}$ content of cement and 1 M NaOH curing solution at 80 °C. The expansion of microlitic dolomite ATJ of Sinian from Tianjin with different particle sizes is shown in Fig. 1. The results indicate that the

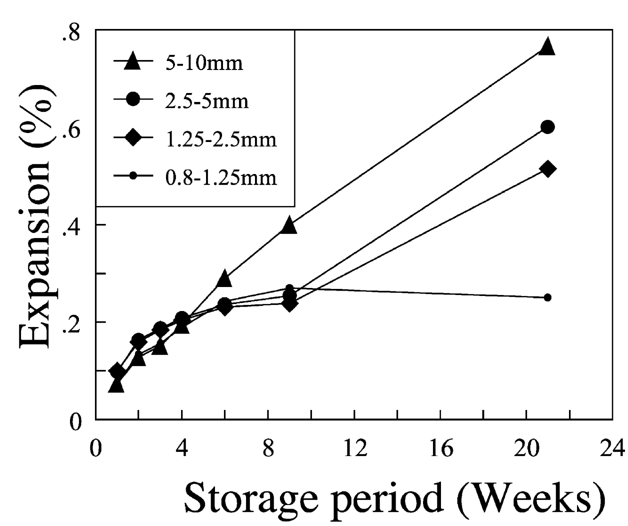

Fig. 2. The expansion curve of dolomitic limestone (LB) from Shandong.

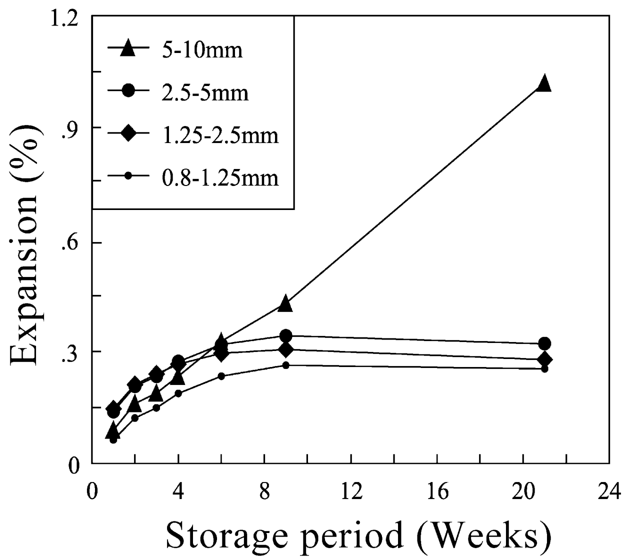

Fig. 3. The expansion curve of dolomitic limestone from Shandong (QJ).

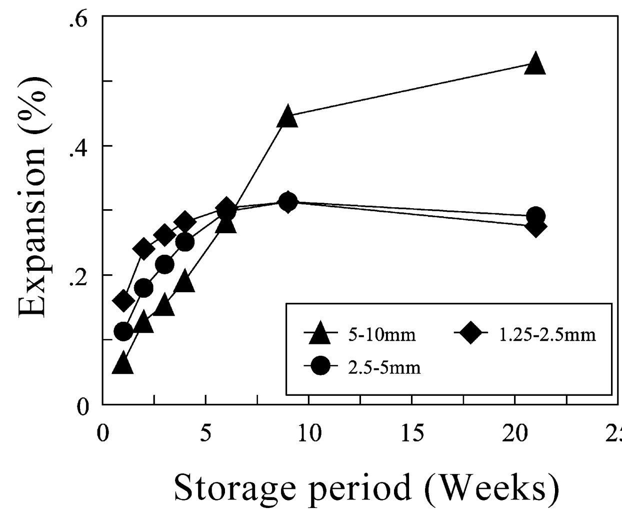

Fig. 5. The expansion curve of dolomitic limestone from Hebei (T3).

expansion increases with increase of particle size. The samples with 5–10 mm particle size show a maximum expansion, and failed by cracking at 6 weeks of age. Furthermore, the expansion curve shows a maximum slope. This phenomenon is quite different from that in ASR.

Fig. 2 shows the expansion curves obtained with dolomitic limestone LB from Lin Qu, Shandong province. It is also clear that the expansion increases with decreasing of particle size at an early age (up to 1 month), but a different pattern appears after 1 month of age. The sample with fine aggregate expands gently after 1 month, whereas the others exhibit a continued expansion pattern. Specimens made with the 5- to 10-mm particles show the largest expansion and slope.

A similar result was obtained with dolomitic limestone QJ from the same site as LB (Fig. 3), but it is from a higher level of the quarry. The structure of QJ is similar to that of the international standard alkali-carbonate reactive rock CK from Kingston, Canada. QJ shows more reactivity and greater expansion than CK. These results indicate that ACR is not only related to the content of clay in the dolomite, but to the structure of dolomite crystals. The results also illustrate that the 5–10 mm particle size is more susceptible to expansion, because the expansion with other particle sizes appears to stop after 5 weeks.

The expansion curve of dolomitic limestone ZK from Sichuan province is shown in Fig. 4. A similar result can be seen, but the alkali-carbonate reactivity of ZK is obviously less than that of QJ. Samples with 5–10 mm particle size show a continued expansion, but the expansion of others level off. The higher sensitivity of particle size of 5–10 mm is also confirmed by this carbonate rock.

Rocks T3 and CK are dolomitic limestones of Ordovician age. The results from T3 in Fig. 5 show that expansion increases with decrease of particle size at early

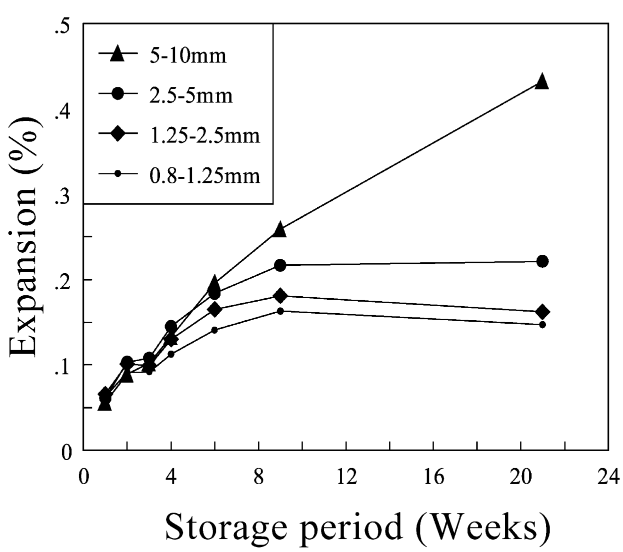

Fig. 4. The expansion curve of dolomitic limestone from Sichuan (ZK).

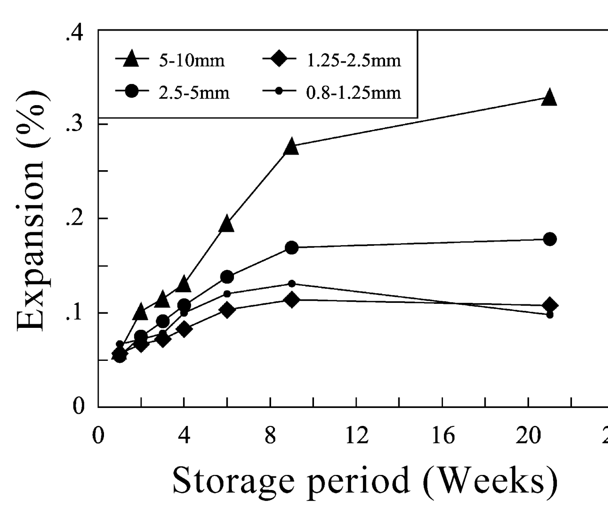

Fig. 6. The expansion curve of dolomitic limestone from Kingston (CK).

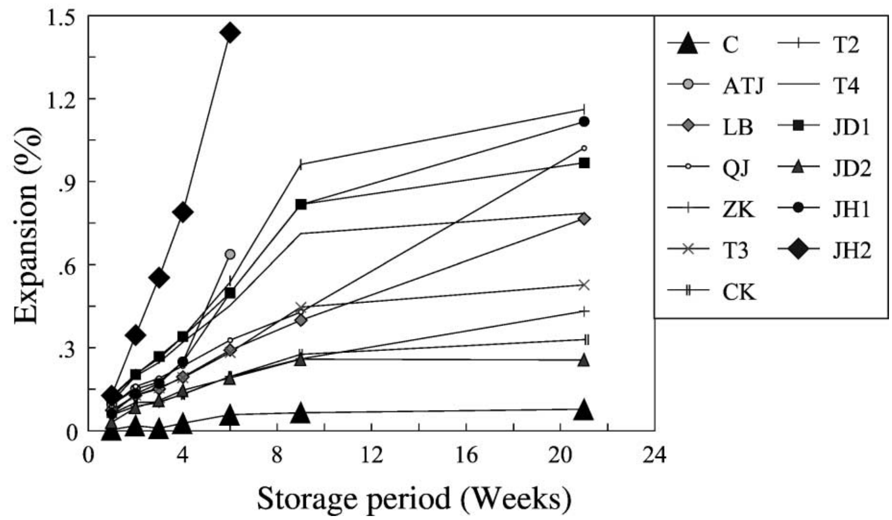

Fig. 7. The expansion curves of various carbonate rocks in alkali solution at 80 °C (1 M NaOH, 5–10 mm size, 40 × 40 × 160 mm).

periods, but levels off after 4 weeks for finer particle size. However, the expansion of sample with 5–10 mm shows a continued expansion as before. The expansion behavior of sample CK in Fig. 6 is similar to that of the other rocks used in this research. It can be concluded that the 5–10 mm particle size is the more sensitive size for ACR expansion for the aggregates used in the present research. It should be noted that for the concrete prism test methods, the larger size of carbonate aggregates may be even more sensitive, and further research works are needed to clarify this point.

Fig. 7 is a summary of the results of this research. It shows the expansion curves of various reactive carbonate rocks, some of which have shown alkali-carbonate reactivity in the field and caused deterioration of concrete structures in many areas, for example, Shandong, Tianjin, Hebei, etc. The control sample C (macromeritic) shows no expansion at any storage period in alkali solution at 80 °C, indicating that heat expansion at this temperature is very small. Normally, macrocrystals expand easily with increase of temperature, so the other finer rocks are unlikely to cause expansion due to heat.

The various reactive carbonate rocks reveal different expansion curves, and the slopes and maximum expansion values of the curves are related to the complex structures and individual chemical and mineral compositions of the respective aggregate. A common phenomenon can be seen where the reactive aggregates with 5–10 mm particle size always show a continued expansion. This leads us to consider how to identify the potential reactivity of carbonate aggregates. Through comparing the behavior of the aggregates in the autoclave method and in field concrete, it can be suggested that if the expansion of the microconcrete bar exceeds 0.1% at 4 weeks, this aggregate can be judged to be alkali-carbonate reactive.

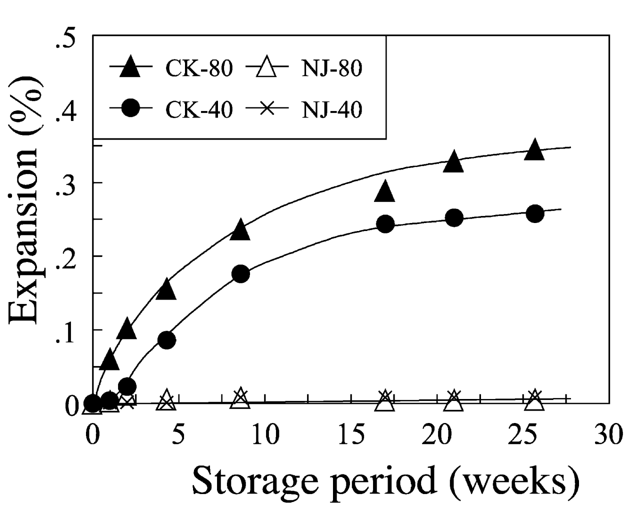

Fig. 8. A comparison test for typical reactive and inert rocks at 80 and 40 °C.

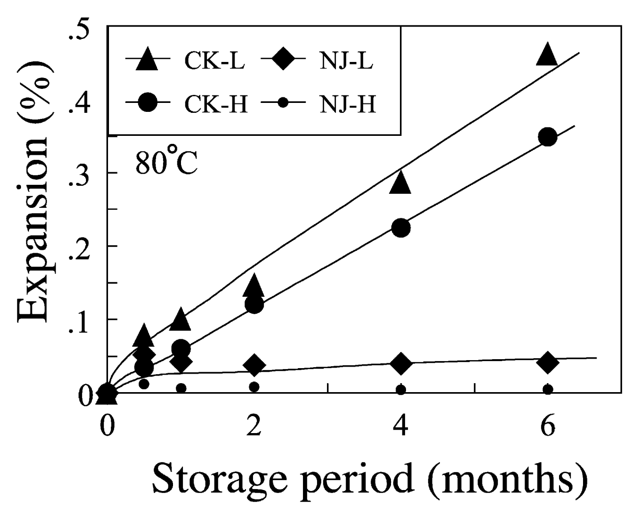

Fig. 9. Comparison of low- and high-alkali cements at 80 °C (40 × 40 × 160 mm).

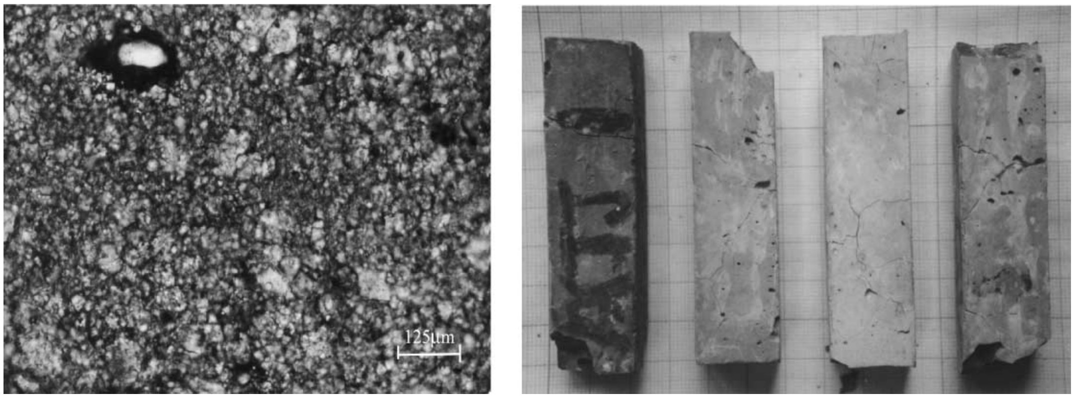

Fig. 10. Mineral structure of ATJ rock and its cracking of mortar specimens (6 weeks).

This judgement can be confirmed by the behaviors in field concrete structures of the test aggregates. The rocks WB, Z, JH and CK from Shandong, Tianjin and Kingston have caused the deterioration of airports, bridges, pavements, railroad ties, and other concrete structures. Furthermore, this judgement is consistent with the autoclave method proposed previously by the authors. It may be reasonable that the test period should be extended to 6 weeks or more for very important engineering projects (e.g., Three Gorges Dam in China), in which the concrete must be durable for several hundred years. It is noted that this judgement naturally needs to be confirmed by testing a wider range of aggregates and by other researchers.

4.3. Influence of test temperature on ACR expansion

As already stated, the two major ways to accelerate AAR are enhancing the content of alkali in the system and increasing reaction temperature. It is noted, however, that the increase of test temperature must not change the nature of reaction products, and not change the process of cement hydration and AAR compared to field conditions. At 80 °C, it is well known that the nature of reaction products and the process of reaction will not be remarkably changed; only the rate of AAR will be accelerated. It is necessary to compare the behaviors of ACR in 1 M NaOH solutions at 80 and 40 °C.

Fig. 8 shows a comparison of ACR test at 80 and 40 °C with the typical carbonate reactive rock CK and inert NJ (pure dolomite, 5–10 mm size). It is clear that the inert aggregate NJ does not show expansion at higher or lower temperatures, meaning that the present test procedure does not cause misjudgement due to heat expansion. On the other hand, standard reactive aggregate CK shows similar sharp expansion curves at 80 and 40 °C. It can be argued that increase of temperature will accelerate ACR, and does not obviously change the mechanism of ACR and the nature of the products. Therefore, the test temperature of 80 °C may be reasonable for identification of the potential alkali-carbonate reactivity of aggregates.

4.4. Influence of cements on ACR expansion

The alkali content of cement is normally believed to be an important factor in controlling AAR. The results of comparative tests for low (0.52% $Na_2O_{eq.}$) and high (1.24% $Na_2O_{eq.}$) alkali content of cements at 80 °C are shown in Fig. 9. It needs to be emphasized that the total alkali content of the test cement is adjusted to the same value (1.5% $Na_2O_{eq.}$) by adding KOH. However, the mortars made with the low-alkali cement cause larger ACR expansion. This phenomenon is also frequently found in ASR testing. Therefore, it is necessary to suggest the low-alkali cement as the standard one, because high-alkali cements may sometimes show an apparent expansion during test period in most of Chinese engineering tests. This phenomenon may be related to the effects of MaO or f-CaO, and a further study is needed. Eventually, the most important note is that the expansion of pure cement paste needs to be tested, and must be less than 0.020%.

4.5. Evidences of deterioration of samples due to ACR expansion

The tested samples were examined by microscopy. Fig. 10 shows the mineral structure of the ATJ rock, and cracking of the specimens made with it after 6 weeks of storage. This mineral structure is similar to that of CK aggregate and contains 20–60 μm dolomite crystals. The aggregate is not susceptible to ASR. After 6 weeks of treatment in alkali solution, all specimens failed by cracking. This fact illustrates that the cracking is caused by ACR expansion, not by other factors.

5. Conclusions

1. The sensitive particle size for identifying the potential alkali-carbonate reactivity is 5–10 mm for the specimen sizes used in the present research. For the concrete prism test, the coarse aggregate size may be more suitable than the 5–10 mm size.

2. At the total alkali content of 1.5% $Na_2O_{eq.}$, the low-alkali cement shows higher expansion than high-alkali cement due to the fact that the former needs a high addition of soluble alkali to reach the same total alkali content. It may be stipulated as the preferred cement in this method.

3. This research offers support for the new accelerated method for determining the potential alkali reactivity of carbonate aggregates. It needs to be internationally examined for more aggregates, and by more researchers.

Acknowledgments

Financial support by the National "Ninth Five Years Plan" for Science and Technology of China is gratefully acknowledged. Special thanks are due to Prof. Zhicheng Huang at the Department of Geology, Nanjing University for his guidance in quarry inspections.

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