



COMPARISON BETWEEN ALKALI-SILICA REACTION AND ALKALI-CARBONATE REACTION

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ABSTRACT

Alkali-aggregate reaction (AAR) may be divided into two kinds: alkali-silica reaction (ASR) and alkali carbonate reaction (ACR). The chemical reaction between the reactive aggregate and alkali will cause serious expansion, and it will result in the deterioration of concrete structures, which is the common character of both reactions. In this paper, the characteristics and differences between ASR and ACR are discussed in detail from the viewpoint of expansive process, mechanism and structural characteristics of the rocks. For ASR, the prime essential is the crystallinity of silica which causes the rocks to display alkali-silica reactivity. Thus only cryptocrystalline, microcrystalline, glassy and strained silica, cristobalite and tridymite etc. display high alkali-silica reactivity. The criteria and methodology to determine the crystallinity of silica are described in more detail. Systematical study shows that for ACR, although the crystallinity of dolomite and the ratio of Ca/Mg of dolomite may influence the rate of reaction, the decisive factors are the size of dolomite crystals and the distribution in the matrix, and the degree of compaction of the surrounding matrix. These results will help to understand more deeply the essential of mechanisms of AAR. In addition, the geological conditions of formation of reactive carbonate rock were studied, which will be very beneficial for confirming the distribution of reactive carbonate rocks in a region or in a country. Finally a method to distinguish between ASR and ACR is introduced.

Keywords: Alkali-aggregate reaction, alkali-silica reaction, alkali-carbonate reaction, microstructure, reactive silica, reactive carbonate rock, deterioration, concrete.

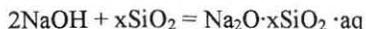
INTRODUCTION

Stanton (1940) discovered that alkali-aggregate reaction could cause expansion and deterioration of concrete. Meanwhile, AAR meant ASR. Since then, alkali-carbonate reaction and alkali-silicate reaction were also discovered. However, up to now, the consistent view is that the so-called alkali-silicate reaction actually is a form of alkali-silica reaction. Maybe it is the microcrystalline quartz scattered in the matrix of rocks, thus some silicate rocks display slow expansion (Tang 1992). For ACR, by comparison with ASR, either the cases of deterioration and the depth and scope of studies are much less than that of ASR. Especially, some scientists have reservations about the truth of ACR who assumed that the expansion might also be caused by the microcrystalline quartz contained in the carbonate rocks. That is to say in essence it also is ASR. Taking these disputes and contradictions into consideration, and recognizing that dolomite rocks are widely distributed in China and a large amount of which is used as aggregate in many important concrete structures, it is absolutely necessary to systematically study ACR. The process of reaction, expansive mechanism and the factors that influence of ACR have been studied from microstructures. For the purpose of necessary engineering practice, we have proposed a method to find the petrographic characteristics of reactive carbonate rocks and the differences between reactive and the non-reactive rocks.

The results provide a scientific basis to guarantee the durability of concrete structures. Through systematical studies and comparisons between ASR and ACR, we concluded that it is beneficial to accurately understand the essential mechanism of ACR and to distinguish ACR from ASR.

ALKALI-SILICA REACTION (ASR)

Reactive silica reacts with the alkali released from cement:



The products display strong absorptivity of water. Its water vapor pressure is far less than that of normal water, and results in great expansion which can be illustrated as:

$$\Delta P = -(RT/V) \ln (P/P_0) \quad (1)$$

In this formula, ΔP -pressure of swelling, T -temperature, V -molar volume of water, P -vapor pressure of $\text{Na}_2\text{O} \cdot x\text{SiO}_2 \cdot \text{aq}$, P_0 -saturated vapor pressure of water at $T^\circ\text{C}$, R -gas constant.

Fortunately, although 80% of the earth is made from silicate minerals, the reactive silica does not involve perfect crystalline quartz and the minerals which contain SiO_2 as a chemical component, such as feldspar, mica, et al. are not expansive, otherwise, it would be very difficult to find full sound aggregates. In general, the so-called reactive silica involve amorphous, cryptocrystalline, microcrystalline and glassy silica, e.g. opal, chalcedony, quartz glass, volcanic glass, crypto- and micro-crystalline quartz and strained quartz as well as cristobalite and tridymite.

ASR mainly depends on the crystallinity of silica. Thus we have to find an accurate method to determine the crystallinity of quartz. Using the optical microscope, it may help to

quantitatively identify the crystallinity of quartz. Fig. 1 shows the classical photos from opal, chalcedony, microcrystalline quartz to coarse crystalline quartz.

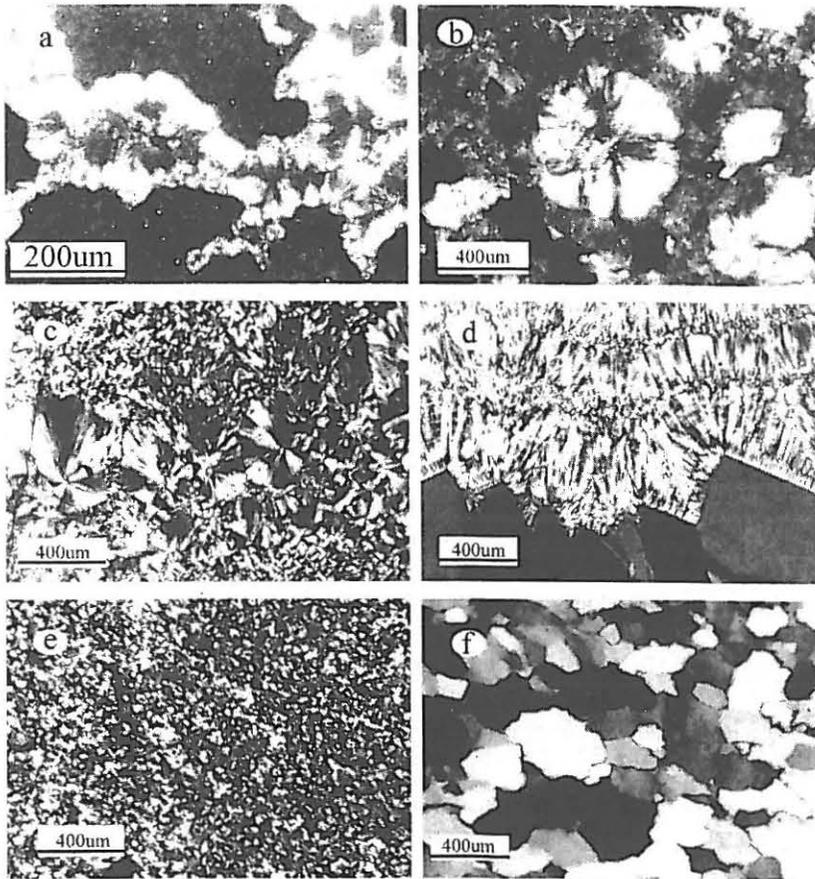


Fig. 1: Several types of silica
 (a) Opal and few chalcedony; (b) & (c) chalcedony,
 (d) Chalcedony + quartz; (e) Microcrystalline quartz,
 (f) Macrocrystalline quartz

In order to quantitatively determine the crystallinity of quartz, DSC (differential scanning calorimetry) was adopted to measure the width of endothermic peak (Tang et al. 1989). The experimental results showed that the alkali reactivity increases with increasing width of the endothermic peak. Another method for evaluation of crystallinity of quartz is positron annihilation technique (Tang et al. 1989), in which the lifetime of capture position (t_2 , picosecond-ps) represents the length of defect. The intensity of capture annihilation (I_2 , %) represents the intensity of long living component, that is the concentration of defect. By experiments, it proved:

$$P \% = 1.06 \times 10^{-3} (t_2 + 10 I_2) - 0.524$$

Where P is the value of expansion obtained by a rapid autoclave test method (Tang et al. 1983).

In order to quantitatively describe the crystallinity of strained quartz, Dolar-Mantuani (1981) suggested to measure the angle of undulatory extinction (UE) and concluded that when the angle is more than 15°, the strained quartz is potentially reactive. However, according to our experiences in the examination of a large amount of rocks which contained quartz taken from various places in China, we discovered that many of them display certain degree of UE, but the alkali reactivities of them were not high. At the same time, there are many kinds of UE, such as curve banding, twist-banding, broomed, lace-like, ring-like, massive, herring-bone, X-type and T-type extinction. Among them, except banding extinction, it is difficult to determine the angle of UE for the other types of extinction. At the same time, Grattan-Bellew (1986) and Andersen and Thaulow (1989) also proved that there is no close correlation between the alkali expansion and angle of UE.

The crystallinity of quartz has been intensively studied by Murata and Norman (1976), who applied X ray diffraction to find a crystallinity index (CI) to quantify the crystallinity of quartz. However, Tong et al. (1997) adopted the profile fitting technique to analyze the quartz's X ray diffraction lines of $2\theta = 66.5-70^\circ$, using the FWHM (full width at half maximum) to evaluate its crystallinity, and found better results between expansion and crystallinity as shown in Table 1. The correlation coefficient may reach 0.95. In Table 1, No.1 is quartz with coarse crystals, No.8 is opal and from No.2-7, the size of crystals is reduced and existing chalcedony.

TABLE 1: FWHM and Expansion of Mortars (P%)

| No. | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|------|--------|--------|--------|--------|--------|--------|--------|--------|
| FWHM | 0.1270 | 0.1357 | 0.1362 | 0.1420 | 0.1525 | 0.1664 | 0.1658 | 0.4997 |
| P % | 0.022 | 0.048 | 0.100 | 0.150 | 0.200 | 0.241 | 0.320 | 1.324 |

Although the chemical compositions of tridymite and cristobalite are the same as quartz, due to the twist of the crystalline lattice, the alkali reactivity is very high. In Japan, the reactive andesite contained cristobalite displays high alkali reactivity. A porcelain sand contained cristobalite also caused high expansion when it was used as aggregate.

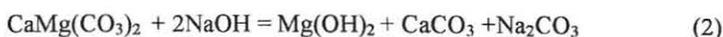
The reactivity of glass contained SiO₂ depends on the chemical compositions (Tang et al. 1986a). As the mole % of SiO₂ (S), Na₂O (N) reduce and the mole % of CaO (C), Al₂O₃ (A) increase, the alkali reactivity of glass reduces. The index of reactivity $K = (C + A) / (S + N)$ might be used to predict the alkali reactivity of glass aggregate. It has been found that as $K < 0.2$, the aggregate is reactive, as $K > 0.3$, non-reactive.

The foregoing discussion illustrates that the alkali reactivity of siliceous aggregates depends on the crystallinity of silica. Amorphous silica is most reactive, the greater the intensity of defects of crystals of silica, the more reactive. Zhang et al. (1990) adopted electron microscope to study the relationship between the defects of crystals of quartz and the alkali reactivity, he found that there is close correlation between them.

ALKALI-CARBONATE REACTION (ACR)

Swenson (1957) first discovered that some concrete deterioration in Canada was caused by ACR. Since then, in Illinois, Indiana, Virginia, South Dakota and Iowa in America, this kind of deterioration also appeared. However, it should be emphasized that it does not mean all carbonates are reactive. In fact, many aggregates made from limestone and dolomite, displayed excellent performance in practice. In Canada, the destructive reactive rocks are the argillaceous dolomitic limestones which display some special petrographic characteristics. The rhombic dolomite crystals ($< 70 \mu\text{m}$) are set in the matrix of very fine calcite crystals ($3\text{-}5 \mu\text{m}$) and clay.

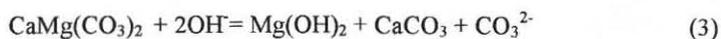
The expansive mechanism of ACR is quite different from that of ASR. The reaction between alkali and carbonate is:



That is "Dedolomitization".

Gillott (1964) believed that, in the above reaction, the solid volume of products was less than that of reactants, thus the reaction of dedolomitization itself could not cause expansion. He concluded that the expansion is mainly due to the uptake of water by the dry clay minerals, which are exposed by the dedolomitization reaction.

The equation (2) may also be described as:



Thus $\Delta G_{298}^0 = -12 \text{ kJ}$.

From a STEM study, most of the clay minerals were found to be present in the matrix of the aggregate but some have been shown to occur in the dolomite; we concluded that the expansion was mainly caused by the topochemical reaction owing to the entry of K^+ , Na^+ and OH^- ions into the restricted spaces and the pressure of crystallization of brucite and calcite (Tang et al. 1986b, Tang et al. 1991, Deng and Tang 1993). The driving force of the above reaction is due to the negative value of free energy (ΔG_{298}^0).

Dedolomitization is a chemical reaction. Of course, it can be expected that there is relationship between the rate of reaction and crystallinity of dolomite. The molecular formula of dolomite is $\text{CaMg}(\text{CO}_3)_2$, among which CaO 30.41%, MgO 21.86%, CO_2 47.3%. The ideal molar ratio is $\text{CaCO}_3:\text{MgCO}_3=1:1$. In the crystal structure of calcite (CaCO_3), one layer Ca^{2+} and one layer CO_3^{2-} are alternately arranged. In the ideal crystal structure of dolomite, Ca^{2+} layers are alternatively replaced by Mg^{2+} layers. Defects of the dolomite crystal might be caused in two ways: (a) in the Ca^{2+} layers a few Mg^{2+} may exist, or conversely some Ca^{2+} ions may proxy for Mg^{2+} ; (b) in the most natural dolomite, the molar percent of CaCO_3 is usually exceeds that of MgCO_3 , up to 7%.

Hadley (1961) studied the relationship between alkali reactivity and the crystallinity of dolomite. He used the ratio of intensities of (110) and (015) of dolomite sample on the X ray diffraction line as the criteria of crystallinity of dolomite. He discovered that the crystallinity

of all dolomite samples, either reactive or non-reactive is not perfect, so he concluded: “dolomite crystallinity would therefore not seem to be an important factor in alkali carbonate reaction”.

Mu (1996) believed that using the ratio of diffraction intensities of (110) and (015) was not suitable, because they are too weak, the intensities of (110) and (015) respectively are the 10% and 8% of that of (104). Mu also used X-ray diffraction, but measured the difference between the position of (104) in the dolomite sample and the standard value d (0.2886 nm) as the criteria of crystallinity of dolomite, and found satisfactory results of relationship between crystallinity and alkali reactivity of dolomite.

Qian (1998) further studied the relationship between the crystallinity of dolomite and its alkali expansion. His experimental results proved that as the dolomite was crushed to below 40-60 μm , i.e. the structure of rocks being destroyed, the rate of reaction and the expansion of compacted mortar bars made from them showed close correlation. That is to say increasing the rate of reaction and expansion correlated increasing degree of disorder in the dolomite crystals. However, further studies confirmed that in test of concrete bars made from 5-10 mm aggregates, the main factor to influence the alkali expansion was the structural characteristics of the dolomite. Some classical photos of petrographic characteristics of dolomite are shown in Fig.2. Fig.2 (a) illustrates the rhombic crystals of dolomite scattered in matrix; (b) mosaic structure of microcrystalline dolomite; (c) oolitic dolomite; (d) mosaic structure of macrocrystalline dolomite.

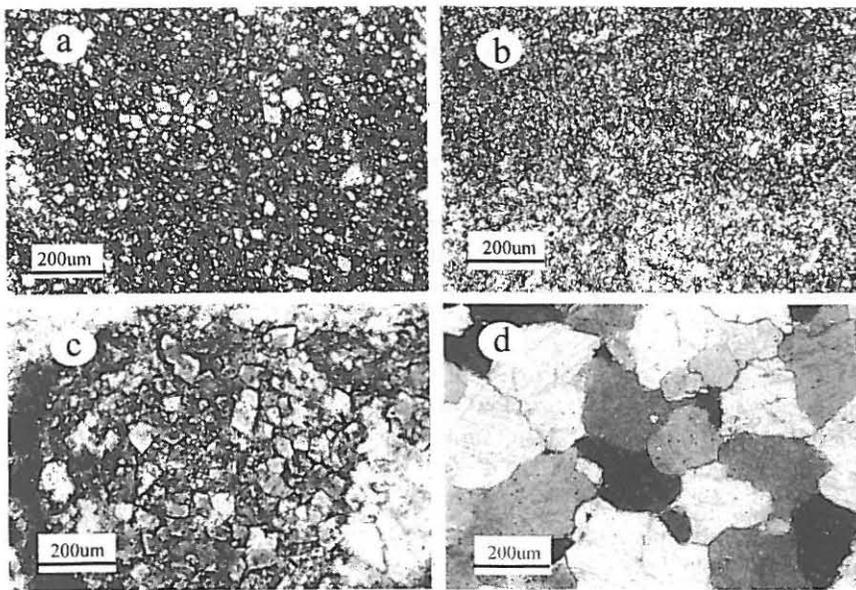


Fig. 2. Petrographic photos of dolomite

Qian (1998) detailed studies of the relations between the petrographic structures and the alkali expansion of dolomite in detail. He concluded that the alkali reactive rocks are mainly dolomite with smaller crystals showing a scattered distribution in the matrix. The

expansivity depends on the crystallinity and size of the scattered dolomite crystals, but the later is more important. At the same time, the structural characteristics of the matrix are also very important. When the matrix is composed of clay or clay and microcrystalline calcite, due to the low porosity and dense environment, expansion is at the maximum. When the matrix is composed of sparite calcite, the porosity of the matrix increases, and the expansion is reduced even though the degree of chemical reaction was the same. As to the macro- and micro-crystalline dolomite with mosaic structure, the chemical reactions took place only in a very thin layer on the particle surface. Consequently, the expansion frequently was not so serious.

It should be emphasized that rocks frequently are not homogeneous, just as shown in Fig.2 (c), for the oolitic dolomite, although only in the oolite, the dolomite crystals being scattered in matrix, large expansion also appeared.

From microfacies, Qian (1998) studied the diagenetic environment, process and the geological characteristics of reactive dolomite. The classical reactive argillaceous dolomitic limestone from Kingston, Canada, was found to consist of calcite bird-eyes, micro-lamination, a small amount of gypsum and pseudomorphs of salt as well as microcrystals of dolomite with disorder. Thus it was concluded that the sedimentary environment for carbonate rocks with high ACR expansivity is one of low energy, shallow marine, higher salinity than normal marine, located next to the edge of ancient continent. Argillaceous dolomitic micrite limestone with high ACR expansivity should be formed in the restricted platform environments, such as the supra-intertidal or lagoon environment. Argillaceous dolomicrites should be found in the supratidal environment which belongs to Sabkha model. The conclusions are illustrated by Wilson's model of facies belts (Fig.3). This is the first time that diagenetic environment is suggested for the formation of reactive carbonate rocks. It is beneficial to predict the distributions of reactive carbonate rocks in a wide region or in a country. Now the map of distributions of reactive carbonate rocks in north China has been established. Through further studies, it may extend to other regions of the world, which will be significant for the purpose of preventing the deterioration of concrete caused by ACR.

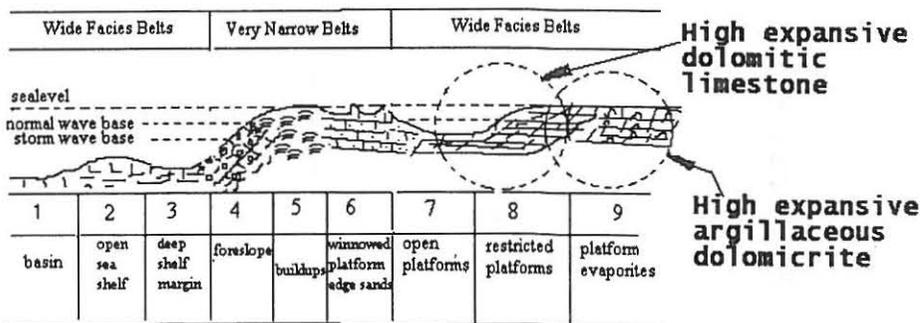


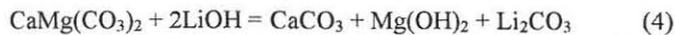
Fig. 3: Facies belts in Wilson's model and possible existing region of rocks with ACR

DISTINGUISHING ASR FROM ACR

In general, carbonate rocks contain more or less amounts of silica. In fact, there are many cases of deterioration of concrete made from carbonate aggregates which contained chert, flint, chalcedony and microcrystalline quartz. Up to now some engineers and scientists still believe that the expansion of ACR might be caused by the reactive silica contained in the carbonate rocks.

Towards this object, some works have been done to confirm that the reaction of dedolomitization itself may certainly cause expansion (Deng and Tang 1993), e.g. using crushed pure dolomite as aggregate, the compacted mortar bar (simulate the dolomite crystals scattered in the matrix of natural rock) also displayed considerable expansion. Additionally the rock cylinders of pure dolomite and magnesite immersed in alkali solution also showed evident expansion. The above evidence fully proves that the reactive carbonate rocks without reactive silica can cause expansion when they react with alkali.

However, in practice, we should determine whether the expansion of concrete structure was actually caused by ASR or ACR, or the ratio of contributions by both. For this purpose, LiOH was selected to differentiate the influences of both. The theoretical base is that LiOH has been proved to be effective to prevent the expansion of ASR, on the contrary, dolomite may also react with LiOH and displays expansion as:



Experiments also proved that this reaction takes place at room temperature even though the rate of reaction is much slower than with KOH. At 0°C, the solubility of LiOH, KOH, and NaOH respectively is 127, 970, and 420 g/L. Although the solubility of LiOH is much lower than that of KOH and NaOH, the saturated solution of LiOH may reach 5.3 mol. Thus it results in a very high pH value which is sufficient to cause the above reaction.

The concrete bars made from reactive carbonate aggregates from Kingston, Canada, were treated at 150°C respectively in 10% LiOH solution (LCK), 10%KOH solution (KCK) and water (PCK), the expansion results are shown in Fig. 4. It illustrates that under selected suitable conditions under which KOH causes expansion due to ACR, so also does LiOH cause expansion. It is an effective measure to differentiate ACR from ASR. Furthermore, it again confirms that ACR itself can cause expansion and cracking.

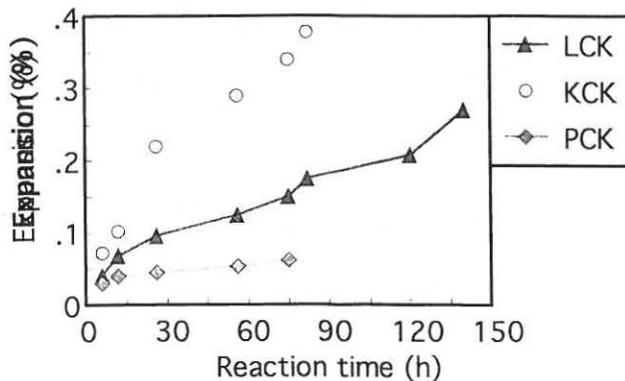


Fig. 4: Expansion of concrete bars in different alkali solutions and in water at 150°C

CONCLUSION

1. The expansivity of ASR mainly depends on the crystallinity of silica.
2. The expansivity of ACR is related to the crystallinity of dolomite, but it mainly depends on the size of the dolomite crystals, conditions of distributions in the matrix and the compact density of the matrix.
3. Argillaceous dolomite micrite limestone with high ACR expansivity should be formed in the restricted platform environments such as sup-intertidal or lagoon environment, argillaceous dolomiticrites should be found in the superatidal environment.
4. Use of LiOH makes it possible to differentiate ACR from ASR.

ACKNOWLEDGEMENT

The authors gratefully acknowledge Dr. P.E. Grattan-Bellew and Dr. C.A. Rogers for sending us the Kingston samples and Prof. J.E. Gillott for his valuable suggestions.

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