

PROGRESS ON THE STUDIES OF ALKALI-CARBONATE REACTION

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ABSTRACT

During the past twenty years, a series of studies on alkali-carbonate reaction (ACR) were carried out by our research group. They include mechanism of reaction and expansion, test methods, deteriorated cases of concrete structures, alkali-carbonate reactivity of carbonate rocks in China, geological conditions of formation of reactive carbonate rocks; distinguishing of alkali-silica reaction (ASR) from ACR. In this paper, the major results were summarized.

Keywords: Alkali-carbonate reaction, Mechanism, Test method, Cases of deterioration, Distinguish method.

1 INTRODUCTION

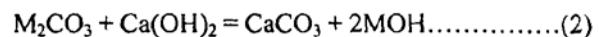
Since Swenson[1] identified the deterioration of concrete caused by alkali-carbonate reaction in 1957, in succession similarly destroyed concrete structures were discovered in the United States (Virginia, West Virginia, Kentucky, Missouri, Tennessee, Iowa, Illinois, Indiana, and New York), Iraq, Bahrain, England, and China. Hansen[2] in 1966, Walker[3] in 1978 and Ozol[4] in 1994 gave comprehensive reviews on this topic. This paper mainly describes the investigative results in the past twenty years on the studies of ACR carried out by the fellows of our research group.

2 MECHANISM OF EXPANSION

The reaction between alkali hydroxide and dolomite can be described as:



Where M represents Na, K or Li. In concrete, the formed M_2CO_3 may react with $\text{Ca}(\text{OH})_2$ from hydration of cement to regenerate alkali:



However, it is not all dolomite aggregates being reactive. There are many concrete structures made of dolomitic aggregates, which displayed satisfactory performance during a long period. Gillott[5] carried out exhaustive petrographic examinations on the reactive carbonate rocks and concluded that only those rocks with special textures were alkali-carbonate reactive. Certain argillaceous dolomitic limestones taken from Kingston, Canada, were highly reactive aggregate. These rocks contain 40%-60% of dolomite or calcite and about 5%-10%

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acid-insoluble residues. Microcrystalline dolomite crystals in 40-50 μ m are distributed in the matrix made of microcrystalline calcite and clays. Even more than 30 years past, this conclusion is still effective and is an important guideline for identifying the potential reactivity of carbonate rocks by petrographic analysis. To illustrate the mechanism of reaction and expansion, we have carried out a lot of research works and get several important results during the past twenty years.

2.1 Topochemical reaction and pressure of crystallization

For equation (1), the sum of the volumes of the solid products is less than that of the reactants, thus Gillott[6] believed that dedolomitization itself could not cause expansion, and the essential reason of expansion was the adsorption of water by dry clays which included in the crystals of dolomite. The dedolomitization just simply developed the channel for access of moisture by clays. However, through repeated examination on the highly reactive Kingston rocks, it confirmed that the clay was not included in the inner part of dolomite crystals, but in the matrix which surrounded the dolomite crystals[7]. The reacted rock sample was polished to thin section and further thinned down by the bombarding with argon ions, and observed with TEM. It was proved that brucite and calcite formed by the reaction were surrounding the dolomite crystals. Therefore, the expansion was caused by the migrating of M^+ and OH^- ions into the restricted space between dolomite crystals and matrix, and by the growing and rearranging of brucite and calcite produced by dedolomitization. From the point of view of thermodynamics, the driving force is negative ΔG . A model of expansion is suggested as shown in Fig. 1.

2.2 Microstructural model of interface II

Frequently there is a reaction rim surrounding alkali-silica reactive aggregates, and usually products of reaction may be found in the interface between the

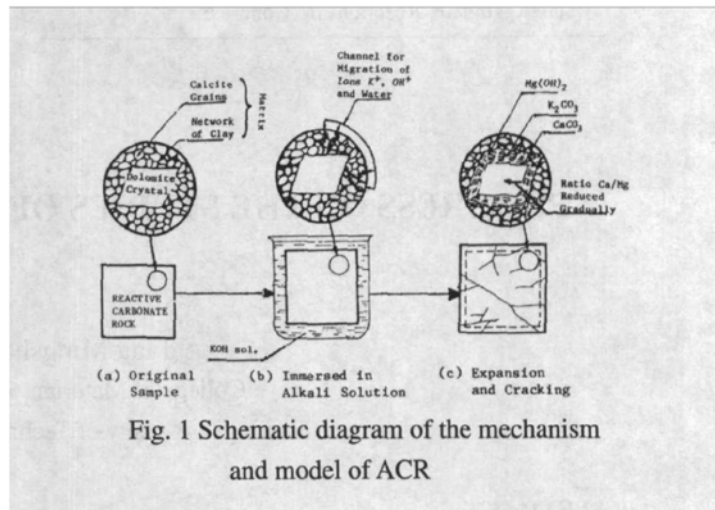


Fig. 1 Schematic diagram of the mechanism and model of ACR

aggregate and cement paste. However, even there is also a reaction rim enveloping the alkali-carbonate reactive aggregates, it is difficult to identify the reaction products of dedolomitization. Therefore, Tong[8] divided the interfaces into two interfaces: interface I is the zone between aggregate and pastes; interface II is the region between dolomite crystal and the matrix (Fig. 2). He emphasized that the dedolomitization is actually carried out in the interface II, where the reaction products of dedolomitization might be identified by detailed examination by SEM.

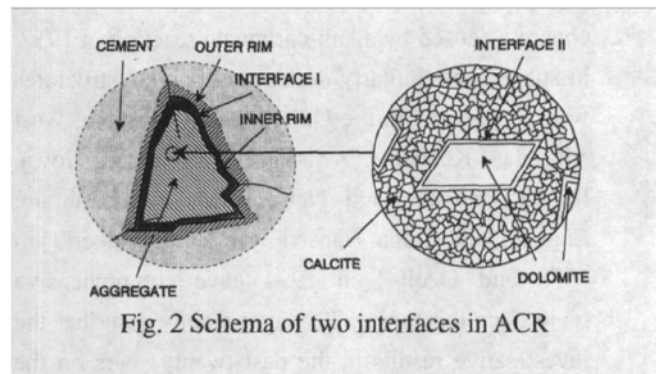


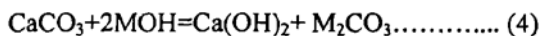
Fig. 2 Schema of two interfaces in ACR

2.3 Compacted tests

As mentioned in the above, the volumes of solid products are less than that of solid reactants in dedolomitization. It is necessary to get direct evidence to identify that these similar reactions might cause expansion in concrete. Compacted tests were projected for this purpose. The tests tried to simulate the environment of rhombic dolomite crystals distributed in matrix of rocks. Samples of pure

dolostone, magnesite and pure limestones were crushed to the size similar to that of dolomite crystals in rocks. They were then mixed with cement and water. The ratio of rock powder/cement was 4:1, and water/cement was 0.1. The mixture was compacted under 300MPa to form compacts in $\phi 10\text{mm} \times 40\text{mm}$.

To avoid the influence of quartz, the rock samples should contain less quartz as possible. Except the dedolomitization reaction, the reactions of magnesite and calcite with alkali are also reactions of solid volume reduction.



Using the data showed in Table 1, the decreases of solid volumes of equations (1), (3) and (4) are 8.6%, 7.4% and 11.8%, respectively. However, all the compacted mortars expanded when cured in 150°C KOH solutions, as illustrated in Fig. 3, Fig. 4 and Fig. 5.

Table 1 Data of products and reactants

Compounds	Molecular weight	Density	Molar volume (cm ³)
CaMg(CO ₃) ₂	184.42	2.87	64.21
CaCO ₃	100.09	2.93	34.16
MgCO ₃	84.33	3.04	27.77
Ca(OH) ₂	74.08	2.34	31.62
Mg(OH) ₂	58.32	2.38	24.50

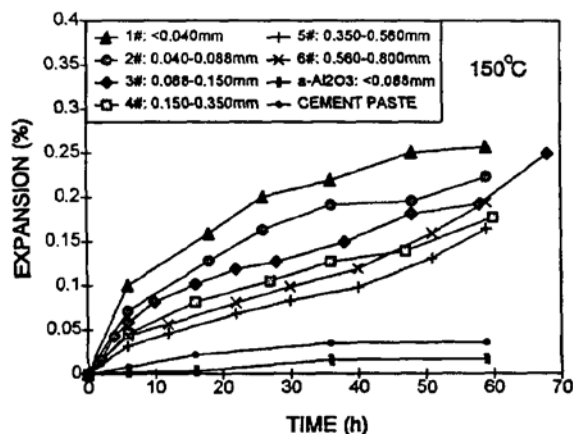


Fig. 3 Expansions of compacts with magnesite powders in different sizes and $\alpha\text{-Al}_2\text{O}_3$ powder autoclaved in 10% KOH solutions at 150°C

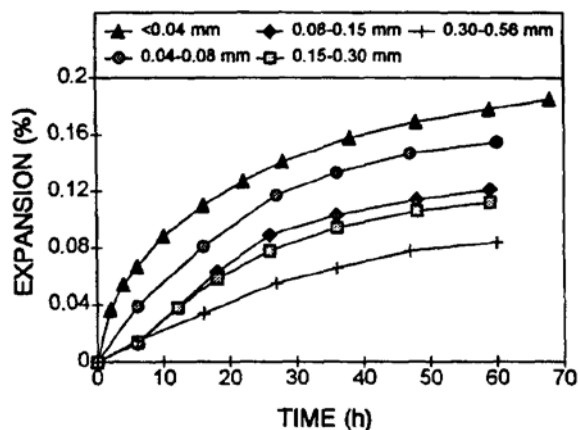


Fig. 4 Expansions of compacts with dolostone powders in different sizes autoclaved in 10% KOH solutions at 150°C

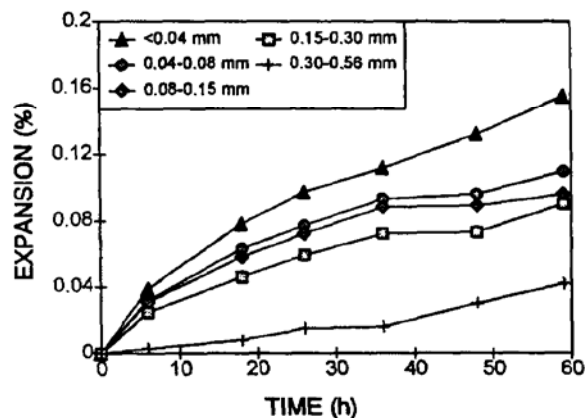


Fig. 5 Expansions of compacts with pure limestone powders in different sizes autoclaved in 10% KOH solutions at 150°C

Fig. 3 shows that reference compacts contained with cement only and Al_2O_3 powder displayed very little expansion. While the compacts made of dolostone, magnesite and limestone powders did expand. These results fully confirm that even the total solid volumes is reduced, under suitable conditions, the expansion still might be aroused by a topochemical reaction and pressure of crystallization.

2.4 Kinetics and thermodynamics

The basic research on the dedolomitization will be beneficial to understand deeply the essential of the reaction. The results of kinetic experiments and

mathematical analysis[9] proved that the rate-determining steps of the dedolomitization are diffusion process and process of nucleation and crystal growth, where the chemical reaction was very fast and is not a controlled factor. The equation of dedolomitization reaction can be rewritten as:



The free energy of the reaction (6) may be calculated by using thermodynamics data, being -12.19 kJ at 298K[10]. The negative free energy means that this reaction is a spontaneous process. This is the driving force to compel Na^+ , K^+ and OH^- ions to be squeezed into the restricted space between matrix and dolomite crystals. It is the theoretical essential foundation of the topochemical reaction. The relationship between pH value and concentration of CO_3^{2-} may be obtained when the reaction is at equilibrium, as listed in equation (7). The results calculated according to equation (7) are shown in Table 2.

$$\text{pH} = 12.93 + 1/2 \lg[\text{CO}_3^{2-}] \dots \dots \dots (7)$$

In the pore solutions of Portland cement pastes, concentration of CO_3^{2-} is always lower due to existing of $\text{Ca}(\text{OH})_2$, which will combine CO_3^{2-} to produce CaCO_3 with very low solubility. Consequently, the dedolomitization might also take place even pH value is not so large. Therefore, ACR cannot be prevented by using low alkali cement and by replacing cement with slag or fly ashes in a normal amount.

3 ACCELERATED TEST METHOD

There are two methods to determine alkali-carbonate reactivity of rocks: the concrete

prism expansion test (ASTM C1105) and the rock cylinder expansion test (ASTM C586). The former requires long period-one year to obtain results, and the later always displays directional expansion, so that the data of length changes vary with the bedding orientation of the rocks. Therefore, ten years ago, we developed an autoclave method for identification of alkali reactivity of carbonate rocks[11], recently modified to an new accelerated method[12]. Through repeated revision, Sommer[13], based on this method, developed a "RILEM AAR-5 rapid preliminary screening test for carbonate aggregates". Grattan-Bellew et al. [14] made a few modifications to this method and use it to identify the alkali reactivity of Canadian classical reactive aggregate, Spratt siliceous limestone (ASR) and Kingston argillaceous dolomite limestone (ACR). Their results confirmed that the modified concrete microbar test had been to be effective in evaluating the potential reactivity of aggregates of both ASR and ACR. They called this method "universal accelerated test for alkali-aggregate reaction".

In this method, the particle size of aggregate is in 5-10mm, and the concrete microbar is in 40mm×40mm×160mm. Ratio of water to cement is 0.3. The specimens are cured in 1mol/L NaOH solutions at 80 °C. Comparison with customary mortar bar test and concrete prism test, the key point of the above method is to adopt only one grade of aggregates. In general, the size grading of aggregates in the mortar bar test method and the concrete prism test method is referred that of strength test method. People believe that it approaches concrete practice. However, it may not be the most sensitive one for identifying the alkali reactivity of aggregate. Experimental results showed that using of one grade of aggregate might frequently be the most sensitive. We should separately consider the potential reactivity of aggregate and the possibility of the actual damage of

Table 2 Relationship between pH value and CO_3^{2-} concentration at the equilibrium of dedolomitization reaction

pH	7	10	11	12	12.5	13	13.5	14
$[\text{CO}_3^{2-}]$ (mol/l)	1.38×10^{-12}	1.38×10^{-6}	1.38×10^{-4}	1.38×10^{-2}	1.38×10^{-1}	1.38	13.8	138

field concrete structures, because it depends on a series of factors such as proportion of concrete, chemical composition of cement and environment. If we want to know whether there is damage of AAR or not in the actual proportion of concrete, perhaps we can use the method (or a modified one) suggested by Criaud et al [15].

4 TEXTURE AND EXPANSION OF ROCKS

“Texture refers to the physical make-up of a rock as distinct from its mineral or chemical composition, in particular to its crystallinity and grain size and to the mutual relationships of the individual components”[16]. Qian[17] studied the relationship between ACR expansion and the porphyrotopic textures of dolomitic limestones in detail. In fact, many dolomite aggregates displayed satisfactory performance and sound durability in practice. The alkali reactivity of dolomite rocks appears to correlate closely with their textures. The texture of classical reactive carbonate aggregates from Kingston Canada is characterized by rhombic crystals of dolomite in smaller than 50 microns distributed in a matrix made of micritic calcite and 5%-25% acid-insoluble residues composed of illite and chlorite. In a sedimentary rock, porphyrotopic means that constituent crystals are of more than one size (inequigranular) and large crystals are enclosed in a finer-grained matrix. Porphyrotopic fabrics are common in dolomitic rocks in which large dolomite crystals set in a fine-grained calcitic matrix. Kingston dolomitic rocks are in a typical porphyrotopic texture. After comprehensive studies of the dolomite aggregates obtained from many places of China, Qian[17] classified the porphyrotopic textures into three kinds(Fig. 6): porphyrotopic-M (6-I and 6-II), psedoporphyrrotopic-M (6-III) and porphyrotopic-S (6-IV and 6-V). The expansion tests proved that the expansibility depends mainly on the size of crystals of dolomite and the characteristics of matrix. The expansion will be larger as the crystals of dolomite

are smaller and the matrix is made of dense micritic calcite than that of porous sparite calcite.

Qian[18] also studied the expandability of dolostone with mosaic textures. It is proved that the expandability of this kind of dolostone was much less than that of argillaceous dolostone. The dolostone is frequently reacted only in the surface to form a reacted rim. However, if it was treated in alkali solutions at 150°C for a long time, it might also display expansion. The expansion decreases as the gap between crystals increases. Perhaps, the larger gap may give less confinement to the growth of crystallization.

The above discussion illustrates that the expandability of carbonate rocks mainly depends on: (a) The size of dolomite crystals distributed in the matrix; (b) Permeability of the matrix; and (c) The degree of compaction of the matrix. Thus, as the matrix is composed of clays or clays and microcrystalline calcite, ACR expansion may be at the maximum due to the low porosity and dense environment. As the matrix is composed of sparite calcite, the porosity of the matrix increases, and the expansion is reduced, even though the degree of the chemical reaction is the same.

From microfaces, Qian [19] studied the diagenetic environment, process and the geological characteristics of the formation of reactive dolostone. It was concluded that the sedimentary environment for carbonate rocks with high ACR expansivity is one of low energy, shallow marine, and higher salinity than normal marine, located next to the edge of ancient continent. Argillaceous dolomitic micrite limestones with high ACR expansivity should be formed in the restricted platform environments, such as sup-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. 7).

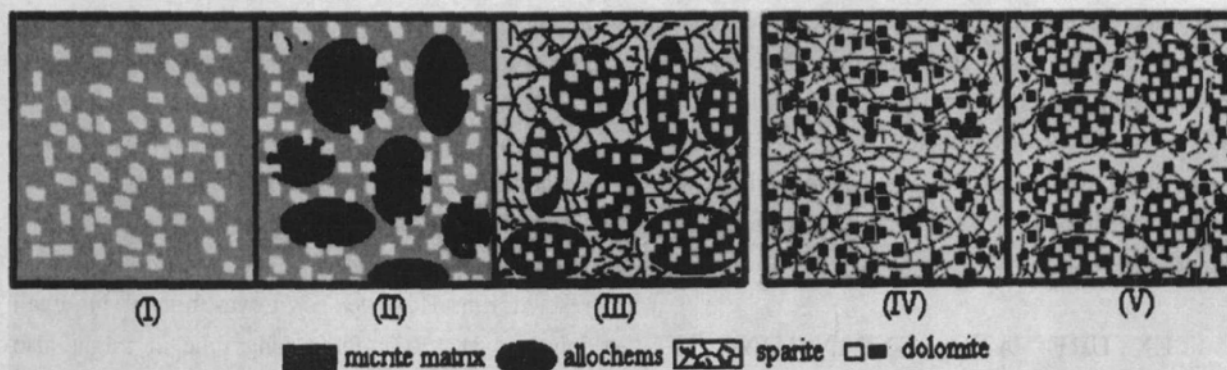


Fig. 6 Different modes of distribution of dolomites in the texture of dolomitic limestones

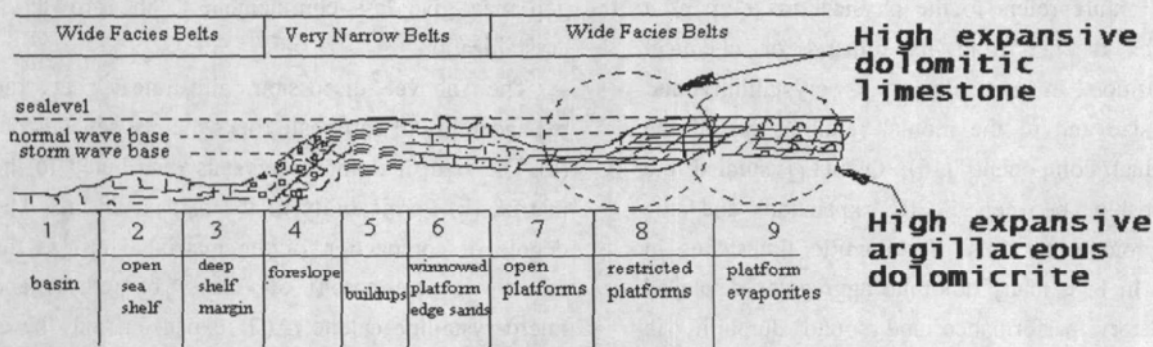


Fig. 7 Facies belts in Wilson's model and region of rocks with ACR

4 CASES OF DETERIORATION AND ACR AGGREGATES IN CHINA

In China, not only ACR has caused deterioration of existed concrete structures such as runway of airport and railway sleepers [20](Fig. 8 & Fig. 9), but also reactive carbonate aggregates were confirmed in the new airport and concrete dam, which will be constructed[21]. The textures of these rocks were very similar to that of Kingston, Canada (Fig. 10 & Fig. 11). All ASTM C295, ASTM C586, CSA A23.2-14A and RILEM AAR-5 proved consistently that the rocks displayed alkali carbonate reactivity.

5 DISTINGUISH ACR FROM ASR

Carbonate rocks usually contain quartz, microcrystalline quartz, or cryptocrystalline quartz. Therefore, it is difficult to confirm the deterioration being caused by ASR or ACR. Through repeated examination by measurement of length change and

microstructural observation under microscope and electron microscope [22], it is confirmed that LiOH could prevent ASR but promote ACR. Fig. 12 shows that alkali-silica reactive perlite did not display expansion even autoclaved in 1.8 mol/L LiOH solutions at 150°C. On the contrary, the reactive carbonate treated under the similar conditions expanded considerably(Fig.13). Thus, we

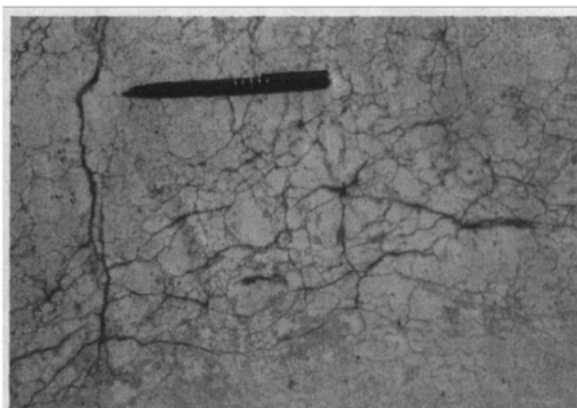


Fig. 8 Pavement of an airport deteriorated by ACR

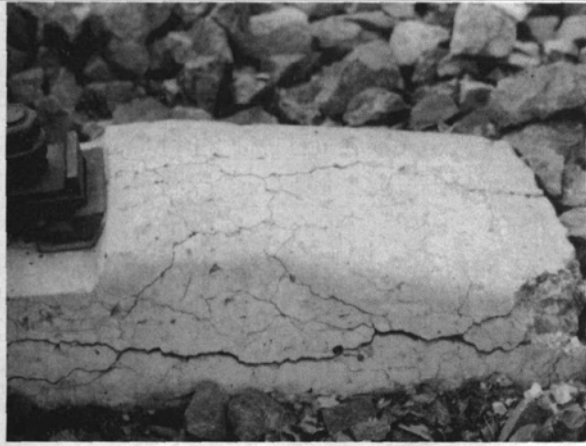


Fig. 9 Railway tie damaged by ACR

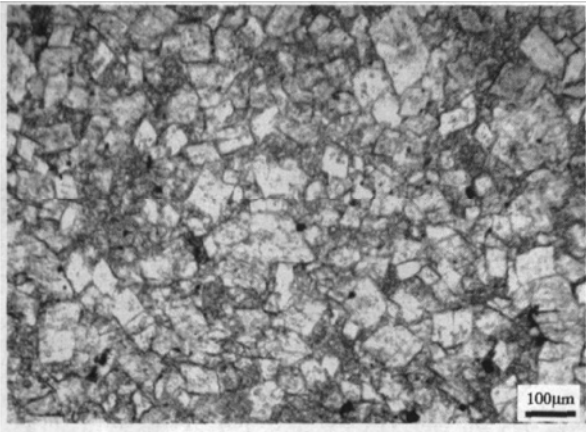


Fig. 10 Microstructure of dolomitic limestone from a new airport

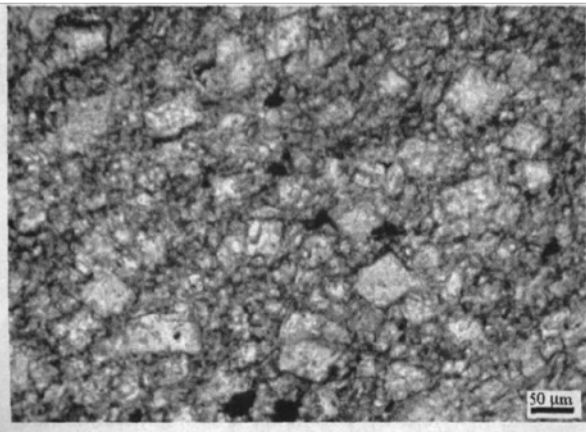


Fig. 11 Microstructure of reactive carbonate rocks from Sichuan province

can adopt LiOH to effectively distinguish ACR from ASR. Especially, we should pay attention to that if the siliceous aggregates contain certain amount of

dolomite, it should be to confirm whether the expansion is also caused by ACR. Mei[22] revealed that the well-known alkali-silica reactive siliceous Spratt limestone from Canada also shows alkali-carbonate expansibility in certain degree.

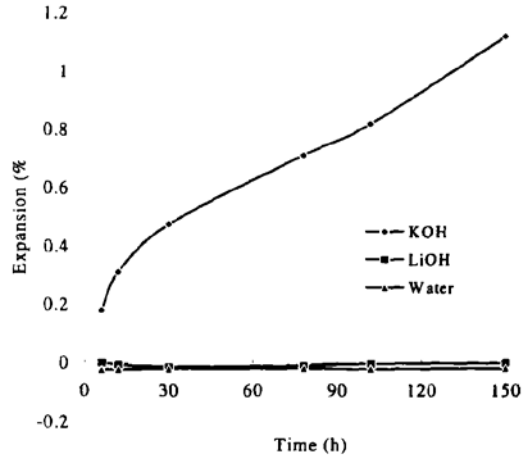


Fig. 12 Expansion of concrete microbars made from perlite in 1.8mol/L KOH, LiOH solutions and water at 150°C

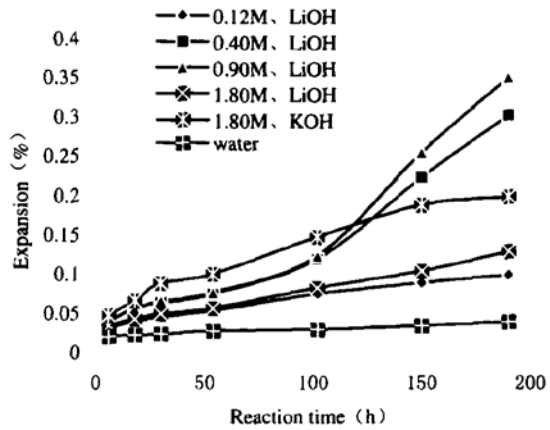


Fig. 13 Expansion of rock prisms made from reactive carbonate rocks in LiOH, KOH solutions and water at 150°C.

5 CONCLUSIONS

1. The expansion of ACR is caused by topochemical reaction and pressure of

crystallization. That means the reactants, OH⁻, M⁺, and water migrating into the restrict space by the driving force of negative free energy and the crystal growth and rearrangement of new products, brucite and calcite.

2. The cracking is caused by the reaction taken place on the interface II between dolomite crystal and matrix rather than that of interfaces I between aggregate and cement paste.
3. Adopting single and larger size (5-10mm) of aggregate, an accelerated test method for ACR was developed.
4. In China, both cases of deterioration caused by ACR and reactive carbonate rocks were discovered.
5. LiOH can effectively distinguish ACR from ASR

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