CLASSIFICATION OF ALKALI-AGGREGATE REACTION

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Up to now alkali-aggregate reactions have been divided into three types: alkal-silica reaction, alkali-silicate reaction and alkali-carbonate reaction. The classification is not only of scientific importance, but of significance also for determining the method of identifying alkali reactivity of aggregate and for searching for preventive measures. The history of the classification of alkali-aggregate reactions, the major characteristics, the expansion mechanisms, test methods, preventive measures are analyzed in this paper. As a result, we suggest that alkali-aggregate reaction is divided into two types: alkali-silica reaction and alkali-carbonate reaction.

INTRODUCTION

Stanton(1)(1940) discovered that alkali could react with some kinds of aggregate and cause expansion of concrete; this being referred to as alkali-aggregate reaction. The reactive components were crypto- or micro-crystalline quartz, strained quartz, volcanic glass, tridymite, cristobalite, chalcedony and opal which consists of amorphous silica or crystalline quartz with a defect lattice. Swenson (2) (1957) discovered some reactive carbonate rocks and Gillott (3) (1973) discovered some reactive silicate rocks (containing phyllosilicates) which could also cause expansion and cracking of concrete. Since then, the alkali aggregate reaction has been divided into three types: alkali-silica reaction, alkali-silicate reaction and alkali-carbonate reaction. However, the silicate reaction was called siliceous rock reaction by Oberholster(4). Recently, in Canadian Standard(CAN3-A23.1, Appendix B2,3)(5), it has been called slow/late expanding alkali-silicate/silica reaction. It seems that opinions on this classification are not consistent and more discussions and analyses are necessary. In the following paragraphs, the history and different views with respect to the classification of AAR are described.

ALKALI-SILICA REACTION

Studies of this reaction are very abundant, and there is no divergence of views with respect to this type, and further discussion, here, is unnecessary.

ALKALI-SILICATE REACTION

Since 1965 Gillott et al.(3) have comprehensively studied the allali-aggregate reaction occurring in Nova Scotia, Canada. The results were published in 1973. The rocks concerned included greywacke, argillite, phyllite, quartzite, schist, and rhyolite. They found that the major characteristics of this kind of alkali-aggregate reaction were quite different from those of traditional alkali-silica reaction as follows: (1).

The expansion takes place very slowly and cannot be detected by ASTM C227.However, the alkali reactive expansion may be obtained by increasing the temperature and alkali content of cement. (2). Alkali silica gel is not common. (3). The experimental results can not be explained by the traditional mechanism of alkali-silica reaction. However by means of petrographic analysis, X-ray analysis and observation under electronmicroscope, it was shown that these rocks contained vermiculite-like minerals with layer structures. Exfoliation of these minerals occurs when they were treated with NaOH solution. For vermiculite-like minerals treated by an alkali solution, the distance between layers increased from 10Å to 12.6Å. Based on these experimental results, Gillott et al. concluded; "There are extractable interlayer precipitates between the basal planes of the vermiculite-like minerals in alkali-expansive Nova Scotia rocks which cause an increse in the volume of rocks"(3).

Oberholster et al.(6) studied the alkali-aggregate reaction occurring in South Africa. The reactive rocks included greywacke, argillite, feldpathic sandstone, phyllite and hornfels. They stated that the change in basal spacing of the K-vermiculite from 10Å to 14Å in the case of ion exchange with Ca or Mg might be one of the factors causing expansion. As for alkali-silicate reaction, Rogers(5) used the terminology late/ slow alkali-silica/silicate reaction involing sandstones and granites containing strained quartz and metamorphosed sediments such as phyllite, argillite, and greywacke, where exfoliation of phyllosilicates would cause swelling of aggregate particles. This is also done in the presence of Na^+ ions and water (7)

There are, however, some disagreements with respect to alkali-silicate reaction. For instance, Diamond (8) reviewed the expansion mechanism of alkali-silicate reaction propsed by Gillott, and stated; "The present writer is inclined to consider this proposal an unlikely hypothesis, at least without more convincing evidence to the contrary". Similarly, when Oberholster (4) reviewed the classification of alkali-aggregate reactions, he did not mention the alkali-silicate reaction. On the contrary, he used "alkali-siliceous rock reaction". The reactive rocks include chert, phyllites, hornfelses, greywackes, quartzites, granites, granite-gneiss and granodiorite gneiss, charnockites and schists. The reactive components are chalcedony, cryptocrystalline quartz and strained quartz. It seems that this reaction is essentially an alkali-silica reaction except for a lower reaction rate compared to the classical alkali-silica reactions invlving opaline material. Grattan-Bellew (9) investigated the expansivity of a suite of quartzwack, argillites and quartz arenites, and he indicated that the expansion had a close correlation with the porosity and content of microcrystalline components(matrix).

Concerning the expansive mechanism of greywackes etc., recently Gillott (10) stated; "There can be no doubt that strained quartz, particularly when fine-grained, will react with strong alkalies and will almost certainly contribute to the expansive reaction. Layer structure silicates and other minerals in rocks of this sort have been shown to be attacked by alkalies and it has been suggested that these reactions may be linked with the expansive mechanism". Here, Gillott indicated the expansion to be caused by both alkali-silica reaction and exfoliation of phyllosilicates

In the modern Japanese Standard(11)(1988), phyllosilicates considered responsibble for alkali expansion are; micro-muscovite (sericite, illite), micro-biotite and vermiculite. If this is the case, then all rocks with these minerals will be regarded as alkali expansive.

For the purpose of determining whether or not the silicate minerals will cause alkali expansion, and what kind of silicate can cause alkali expansion, more than a hundred silicate minerals, including nesosilicates, inosilicates, tektosilicates and phyllosilicates, were examined to study their alkali reactivities by Tang et al.(12). Twenty three minerals were examined by the autoclave rapid method proposed by Tang et al. (13).The results of expansion are shown in Table 1.

After treatment by alkali solution under autoclave conditions, some mortar samples were examined under microscope to investigate the degree of reaction(see Table 1). According to our experiences, if the expansion of sample treated at 150℃ is greater than 0.1%, the aggregate is reactive. From Table 1, it can be seen that the expansion values of all silicate minerals are far less than 0.1%, except for glauconite (0.104%). Careful examination under microscope showed that this sample of glauconite contains microcrystalline quartz and chalcedony. The expansion of this sample is partially caused by alkali-silica reaction. Petrographic examinations proved that majority of silicates could be attacked by alkali(especially at 200℃), just as shown by Gillott[3]. But the values of expansion are not great enough to be deleterious. Moreover, when

TABLE 1-Expansion of Mortar Bars Made With Aggregates of Silicate Minerals autoclave-treated at 150℃ or 200℃ for 6 hours

No.	Class	Name of minerals	Expansion (%) 150℃,6h.	Degree of reaction	Expansion (%) 200℃,6h.	Degree of reaction
1	Nesosilicate	Olivine	0.040	A	0.059	A
2		Andalusite	0.043	A	0.071	A
3		Kyanite	0.048	A	0.094	A
4	Inosilicate	Augite	0.065		0.063	A
5		Actinolite	0.062		0.060	A
6		Hornblende	0.045		0.048	A
7	Tekiosilicate	Orthoclase	0.026	D	0.012	B
8		Albite	0.031	D	0.032	B
9		Microcline	0.015		0.032	
10		Nepheline	0.031		0.032	
11		Leucite	0.043		0.046	
12	Phyllosilicate	Pyrophyllite	0.054		0.051	
13		Serpentine	0.051		0.067	
14		Illite	0.042		0.055	
15		Glauconite	0.104		0.166	
16		Chlorite	0.032	C	0.040	A
17		Talc	0.039		0.059	
18		Muscovite	0.027	D	0.029	D
19		Biotite	0.035	D	0.046	D
20		Zinnwaldite	0.037	D	0.049	D
21		Kaolinite	0.035	C	0.048	C
22		montmorillonite	0.069	C	0.079	C
23		Vermiculite	0.021	D	0.024	D

Note: A-Totally reacted; B-Partially reacted;
C-Slightly reactly; D-Unreacted.

treated at 300℃ in alkali solution, corundum was severely attacked. The expansion of specimen containing corundum was still smaller. It is possible that the water absorptivity by the products of reaction of these minerals is not strong. Our past research (14) indicated that increasing the conents of CaO and Al_2O_3 and correspondingly decreasing the contents of SiO_2 and Na_2O would considerably reduce the water absorptivity by the products of synthetic glass. In kyanite (Al_2O_3 2SiO2), vermiculite [$(Mg, Fe, Cl)_3(Al, Si)_4O_{10}(OH)_2 4H_2O$], and other silicate minerals the content of SiO_2 is relatively low and the amount of Al_2O_3, MgO, Fe_2O_3 etc. is relatively large, the water absorptivity of the attacked product might not be obvious. In addition, various kinds of aggregate, phyllite, argillie, zeolite etc. were examined by Tang et al. [12], and it was found that expansion depends on the content of microcrystalline quartz and chalcedony rather than that of phyllosilicate.

Based on the above discussion, it is concluded that alkali-silicate reaction is actually an alkali-silica reaction, and the rate of expansion depends on sizes and defects of crystals of quartz and the distribution state of microcrystalline quartz. Consequently, rocks without phyllosilicate may also display slow expansion. When fine crystals of quartz are distributed in other minerals(even carbonate) or mixed in the matrix, the Na^+, K^+, OH^- ions must pass through a long distance and overcome high resistance to reach the surface of reactive particles, and as result, the reaction may be delayed. Gillott[14] has shown that a dense, intergrown microstructure may delayed alkali-aggregate reaction. Recently, Criaud [16] confirmed that autoclave rapid method proposed by Tang et al. could be used for both alkali-silica reaction and alkali-silicate reaction. Grattan-Bellew[17] confirmed that the rapid method proposed by Oberholster might also be used for both reactions. These results indirectly suggest that both reactions are essentially similar.

ALKALI-CARBONATE REACTION

Swenson(2)(1957)first discovered that the damage of concrete structures near Kingston, Ontario, Canada, was caused by alkali-carbonate reaction. Swenson. and Gillott(18) confirmed that the reactivity of reactive carbonate rock could not be determined by mortar bar test (ASTM C227) but could be identified by using concrete prisms. They also showed that rock prisms might rapidly expand in alkali solution, leading to development of the rock cylinder test(ASTM C586) to identify the alkali reactivity of carbonate rock.

Through the comprehensive investigations of Swenson, Gillott (18) and Hadley (19) on the microstructure of reactive rock, it was proved that reactive rocks are typically argillaceous dolomitic limestones which display some special petrographic characteristics. The rhombic dolomite crystals($<70\ \mu m$) are set in matrix of very fine calcite crystals(3-5 μm) and clay. In general, the content of insoluble material is 5-20%, dolomite 40-60%. The clay mineral is illite or chlorite. Cases of destruction by alkali-carbonate reaction were also discovered in America and the Middle East.

According to the experimental results of volume change, absorption of water and the powder cell test, Gillott(20) explained the expansive mechanism of alkali-carbonate reaction as follows: "(1).Alkali attack on the dolomite crystals releases included clay in an "active" state with an unwetted surface(2). Some of the Ca_2^+ and Mg_2^+ ions probably present on exchange sites are replaced by Na^+ ions. (3) Development of a hydrated double layer made up of oriented water molecules, and cations near the newly exposed clay surface, and anions further from the surface.(4). Development of the double layer and accompanying hydration processes cause the water uptake, which leads to expansion". In the reaction of dedolomitization,

$$CaMg(CO_3)_2 + 2MOH \longrightarrow Mg(OH)_2 + CaCO_3 + M_2CO_3$$

the sum of volumes of solid products is smaller than that of the reactants. So far, Gillott(19) believed that reaction of dedolomitization itself cannot cause expansion and concluded that the expansion is essentially due to the uptake of water by the clay minerals, which is exposed as result of the dedomitization reaction.

According to the experimental results by Hadley(19), a single crystal of dolomite treated in alkali solution for up to 100 days, expanded by 0.15%. At the same time, the clay matrix might act as a semipermeable membrane and cause osmotic pressure. The matrix composed of fine calcite and clay is the weakest link which can be easily broken.

We studied the microstructures of reactive carbonate rocks of Kingston, Canada in more detail(21). It was confirmed that brucite was formed on the surface of rhombic dolomite crystals and calcite formed in the original surface layer of dolomite crystals. Accordingly, we proposed that expansion is caused by topochemical reaction and pressure of crystallization. It is well known that rhombic crystals of dolomite are closely surrounded by matrix of clay and calcite. The intrusion of K^+, Na^+, OH^- ions and water molecules into these restrained spaces can certainly cause expansion. Although the volume of solid products is smaller than that of reactants, the total volume after reaction would be greater than that of the original volume occupied by a dolomite crystal due to addition of the volume of these intrusive ions and molecules. Furthermore, the newly formed brucite and calcite will rearrange and produce crystallization pressure. In a concrete sample damaged by alkali-carbonate reaction from Corwal, Canada, it was found that the cracks pass around the surface of dolomite crystal, but never through dolomite itself (22). According to these phenomena, we finally proposed an expansion model mentioned above. Thermodynamic calculation shows that ΔG^0_{298} of dedolomitization reaction is negative, -12.19kJ, which is a chemical driving force for the intrusion of ions.

Dedolomitization reaction may be also written as follows:

$$CaMg(CO_3)_2 + 2OH^- \longrightarrow Mg(OH)_2 + CaCO_3 + CO_3^{2-}$$

According to this equation, reaction may be aggravated with increasing OH^- ion concentration and reducing CO_3^{2-} ion concentration. By using buffer solutions with various pH values to study the dedolomitization reaction, the above conclusion was proved(22). From this point of view, the role of $Ca(OH)_2$ was discussed and the approach to minimize the damage by alkali-carbonate reaction was noted. Hadley(19) has suggested that $Ca(OH)_2$ may regenerate alkali:

$$Na_2CO_3 + Ca(OH)_2 \longrightarrow NaOH + CaCO_3$$

Here we emphasize that beside the action of regeneration of alkali, $Ca(OH)_2$ may reduce the concentration of CO_3^{2-} ions, which increases the driving force of dedolomitization. Similary to the case of alkali-silica reaction, $Ca(OH)_2$ also plays an important role in promoting alkali-carbonate reaction.

Many experimental results showed that unlike the case of alkali-silica reaction, using low alkali cement or mineral admixture cannot effectively prevent alkali-carbonate reaction. According to the correlation between pH value and dedolomitization reaction(22), it can be expected that for the purpose of minimizing alkali-carbonate reaction, the pH value of pore solution of cemet paste should be much lower than that for preventing alkali-silica reaction. Thus we suggested using low alkali cement (<0.4%) and high volume of fly ash to avoid alkali-carbonate reaction.

CONCLUSIONS

It is suggested that alkali-aggregate reactions be divided into two types: alkali-silica reaction and alkali-carbonate reaction. For development of test methods for identifying alkali reactivity of aggregate, alkali-silica may be divided into rapid and slow types. It seems unnecessary to separate an unique type, alkali-silicate reaction. However, the influence and role of exfoliation of phyllosilicates by attack of alkali needs study further.

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