Observation Around the Cracked Region Due to Alkali-Aggregate Reaction by Analytical Electron Microscope

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I. INTRODUCTION

Recently, the deterioration of concrete structures due to the alkali-aggregate reaction(AAR) has become of major interest for many investigators in various scientific fields.

It is generally recognized that deterioration of concrete due to a sluggish expansion would be caused by the AAR which produces a swelling gel in the presence of water. However, the reaction does not depend on the 'Mass Action Law', but the maximum expansion is observed at a specific proportion of reactive aggregate or at a limitted alkali content which is known as 'pessimum proportion'. Due to this peculiarity, evaluation of aggregates to predict their alkali-silica reactivity is technically difficult.

This work was conducted, as a fundamental study, to understand the reaction mechanism by comparing the crack development with distribution of constituent elements such as Si, Ca. Na, and K using electron microscopy with analytical equipment.

Prior to the micro-observation, physico-mechanical properties were measured for the cement mixtures with different kinds of aggregate and different alkali contents, and the effect of an addition of granulated blast-furnace slag on the AAR was examined.

II. EXPERIMENTAL

1) Materials

Table 1 shows the chemical composition of ordinary Portland cement(OPC) and granulated blast-furnace slag(slag) used in this experiment.

Table 1 Chemical Composition (wt.%)

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	Na_2O eq.
O P C	21.6	4.9	3.0	64.7	1.7	2.2	0.44	0.62	0.85
Slag	43.7	13.0	0.23	40.8	5.9	0.0	0.31	0.45	0.61

Four kinds of natural minerals were used as aggregates. The density of these was about 2.6 g/cm^3. The relative quantities of these minerals estimated from X-ray diffraction analysis is shown in Table 2.

Table 2 Relative Quantity of Minerals in the Aggregates

Aggregate	Albite	Quartz	α-Cristobalite
(A) Pyroxene andesite(hypersthene)	+++	none	++
(B) Pyroxene andesite(bronzite)	++	++	+(?)
(C) Mud stone	+	+++	+(?)
(D) Sand	none	+++++	none

2) Measurement of expansion coefficient and dynamic elastic modulus

Grain size distribution of the aggregates and their amounts by weight are as follows: 0.15 - 0.3mm : 0.3 - 0.6mm : 0.6 - 1.2mm : 1.2 - 2.5mm : 2.5 - 5.0mm = 3 : 3 : 5 : 5 : 4.

Mortar bars were prepared by mixing according to the prescriptions shown in Table 3.

Table 3 Mixture Proportion

NO.	Flow value (mm)	Slag (%)	NaOH(%) in mixing water	Unit Weight(kg/m³)			
				W	Port.Cem.	Slag	Aggregate
1	203	0	0	306	612	0	1224
2	193	0	2	306	612	0	1224
3	186	0	4	306	612	0	1224
4	188	0	5	306	612	0	1224
5	183	30	5	306	428	184	1224
6	182	50	5	306	306	366	1224
7	187	70	5	306	184	428	1224

Conventional measurements of the physico-mechanical properties with time of curing at 50°C which was carried out for three test pieces having a dimension of 4 x 4 x 16(cm). The results are shown as an average value of three measurements. The ratio of water to cement was fixed at 0.5 by weight for all preparations.

3) Mortar specimen for microscope observation and analysis

In order to minimize the surface damage and to avoid the effects on water-soluble element as much as possible, cutting was conducted by a fine diamond-impregnated wire saw without any coolant, followed by surface polishing. For the purpose of comparison of preferential exolution of the resulting alkaline silicate gels, two kinds of diamond paste suspended in water or oil were used as polishing agents for the small pieces cut from an identical reacted mortar bar.

Electron microscope(SEM) observation and measurement of the distribution of selected element(EDS and EPMA) were done using JEOL JCXA-733 with accelerating voltage of 15 kV. The electron micrographs thus obtained indicates not only the morphological characteristics and crack development, but also the average atomic number of dispersed grains on the basis of the variation in their brightness.

III. RESULTS and DISCUSSION

1) Effect of experimental conditions on the physico-mechanical properties of mortar

As would be expected, the physico-mechnical property depends markedly on the reactivity of aggregate.

In particular, as shown in Figs.1 and 2, Pyroxene andesite(A) is very

reactive and causes marked expansion and a lowering of the dynamic elastic modulus. All test pieces with different aggregate were made by mixing with 5 % NaOH solution(NO.4 in Table 3).

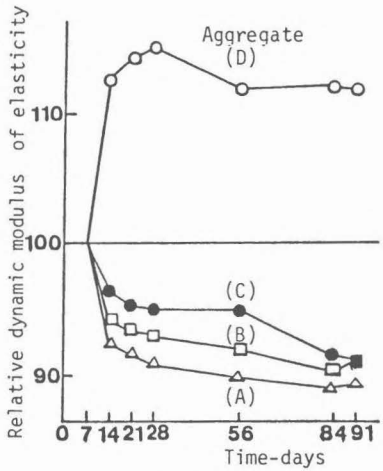

Fig. 1 Dependence of aggregate reactivity on relative dynamic modulus of elasticity standarized on 7 days measurement

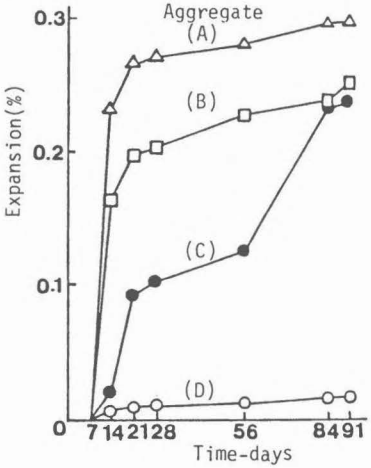

Fig. 2 Dependence of aggregate reactivity on expansion

Expansion characteristics shown in Fig.2 are related approximately to the amounts of α-crystobalite and albite in each aggregate.

In general, the rate of reaction, which is controlled by diffusion process at the solid interface, is accelerated for fine powders with an active surface. To examine the effect of aggregate size on the expansion behavior, an experiment was done with two mixtures containing aggregate(A) of less than 0.15 mm and of 0.15 - 5 mm in diameter, respectively, as shown in Fig.3. The significant difference between the expansion of mortar bars containing the fine and coarse reactive aggregates was observed.The lack of expansion of mortar containing reactive aggregate of grain size <0.15 mm is probably due to the pozzolanic reaction occurring with finely ground reactive aggregate.

A decrease in the alkali content of mortar bars causes a decrease in expansion coefficient as illustrated in Fig.4.

Extensive studies have been carried out to suppress the deterioration of concrete by adding various kinds of inhibitors. In this study, the effect of slag addition on the expansion tendency of mortar containing Pyroxene andesite(A) which is very reactive was examined. The results in Table 4 show

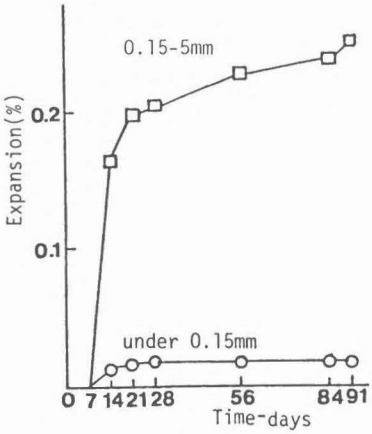

Fig. 3 Dependence of expansion tendency on grain size of aggregate

the relative expansion(%) of mortar bar containing slag compared to mortar bars made with 100% Portland cement.

As shown in Table 4, slag addition was effective in reducing expansion without any deterioration. Absorption of alkali by the hydrating slag may be the reason for the reduced expansion which was observed in mortar bars containing slag.

Further systematic investigation is essential to elucidate the mechanism of the slag reaction by analyzing the chemical reaction between alkali and slag.

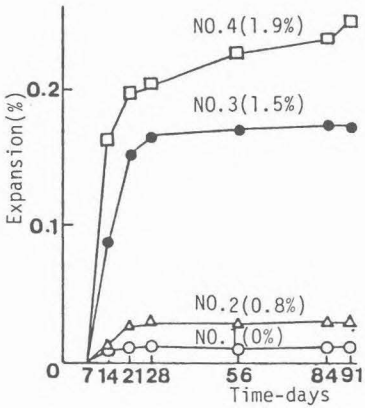

Fig. 4 Effect of alkali content of mixing water(%) on expansion

Table 4 Relative Expansion, during Curing, and Mechanical Strength after 230 days, of Mortar Bars

NO.	Slag (%)	Relative Expansion after curing time(days)				Mechanical strength(kg/cm²)	
		14	28	50	91	Bending	Compressive
4	0	100	100	100	100	55.2	322.2
5	30	50	63	65	68	56.2	350.7
6	50	40	42	48	48	66.5	374.4
7	70	20	28	25	22	68.3	403.1

2) Observation by electron microscope

The very reactive specimen made with aggregate(A) was chosen for micro-observation. Little difference was found between specimens prepared using various polishing technique.

The following observation was carried out for the oil-polished specimen.

Figure 5 illustrates an unreacted part of Pyroxene andesite(A). A large portion of the mineral is composed of prismatic albite crystals having 3 - 10 x 10 - 50 μm in dimension. Interstitial material between the albite crystals, shown as an agglomerate of fine particles was identified as Oligoclase. Whitish crystals were Hypersthene and Ilmenite as indicated in Fig.5.

Figure 6 shows a selected section at low magnification illustrating fracture development.

Figure 7 is a magnified detail SEM of a part of Fig.6 showing a deposit precipitated at the terminal of

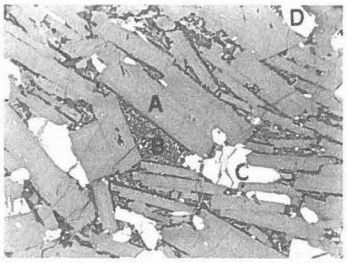

Fig. 5 SEM of Pyroxene andesite(A)

A : Albite	$NaAlSi_3O_8$
B : Oligoclase	$(Na,Ca)(Al,Si)_4O_8$
C : Hypersthene	$(Mg,Fe)SiO_3$
D : Ilmenite	$FeTiO_3$

(bar : 10 μm)

a crack. Distribution of elements such as Si(Fig.8), Ca(Fig.9). Na(Fig.10), K, Al, Mg, and Fe was analyzed in this section by EPMA method.

A critical examination of Figs.7 - 10 shows that;

(1) Cracks generated at an interface of an aggregate expand toward cement mortar and terminate near the boundary of another aggregate.

(2) Deposition of an alkaline silicate gel to explain the penetration of crack is not recognized from the variation in those element concentrations.

(3) Ca-bearing compound is, however, clearly observed at the end of the hair cracks as a long and narrow deposition. Similar deposition is also recognized at the circumference of larger cracks.

(4) The dark ring around the small grain is not composed of silicate gel but an intermediate hydrated calcium silicate containing a small amount of Al and S.

It is very difficult to conclude the mechanism of the AAR from the experimental results described above, but the fact of (3) suggests that a behavior of Ca-bearing compound deposited locally would have a key to explain the mechanism.

Deposition of $CaCO_3$(Calcite) on the surface of reacted bar has been reported with relation to the alkali-silica reaction. The transportation of Ca ion would be accompanied by the exolution of Na_2O - SiO_2 gel of low viscosity followed by the carbonation reaction in air with release of the fluid gel to the surrounding.

Consequently, it can therefore be presumed that the formation of an alkaline silica gel containing a proper amount of Ca ion would be a trigger to cause the AAR.

Acknowledgement

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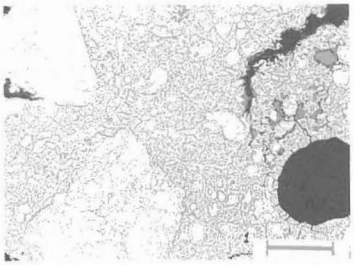

Fig. 6 SEM illustrating a crack development (bar : 0.1mm)

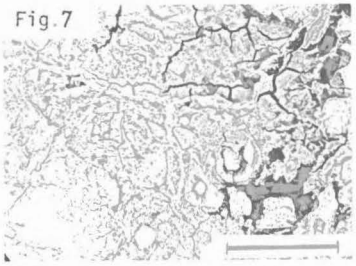

Fig.7

Fig.8 (Si)

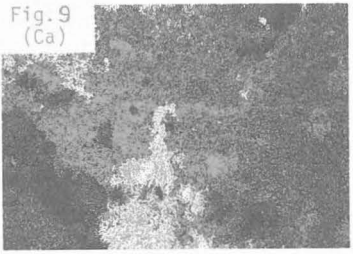

Fig.9 (Ca)

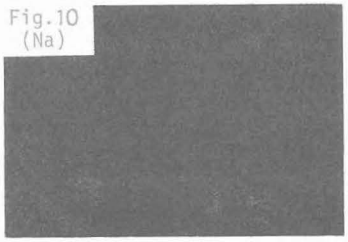

Fig.10 (Na)

Figs. 7 - 10 SEM and EPMA
Fig. 7 SEM of polished surface of reacted mortar bar (bar : 0.05mm)
Fig. 8 Si distribution by EPMA
Fig. 9 Ca distribution by EPMA
Fig.10 Na distribution by EPMA