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A FEW REMARKS ON ALKALI-REACTIVE CHERT AGGREGATES

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1. INTRODUCTION

A number of concrete structures in Japan have been shown to have deteriorated as a result of an alkali-silica reaction between chert aggregates and alkalis from the cement paste. To clarify the characteristics of alkali- reactive cherts, thirty chert aggregates taken from nine pieces of deteriorated concrete were examined macroscopically and microscopically, by X-ray diffraction analysis and by differential thermal analysis.

2. MACROSCOPIC AND MICROSCOPIC OBSERVATION

2-1 Occurrence of the Products of Alkali-silica Reaction

Nine hand specimens of deteriorated concrete were sawed to obtain a new surface and activated alkali-silica reaction in water. Reaction products in the form of white gel exudates develop in the boundary between cement paste and alkali reactive aggregates (photo 1.a, b.)[1]. A small amount of gel fills crack in cement paste, but it is relatively poor in the inner part of the chert particle (photo 1.d). Dark rims, a change in the original composition of aggregate, are often found within the outer of part of chert aggregates (photo 1.c). No particular change is observed in the alkali-silica reaction in some particles of chert aggregate.

2-2 Microscopic Examination

Microcracks and a small amount of gel within and adjacent to expansive aggregates may be visible in thin sections under a polarizing microscope. However, the gel is difficult to identify in thin sections because the gel is usually translucent, white and isotropic microscopically. Herein the dyed thin section was examined under a microscope on the concrete cores. As shown in photo 2, the microcracks and reaction products dyed red were identified easily[2]. The aggregates develop an irregular form of cracking. The reaction products form fillings of irregular shapes within three parts of expansive chert aggregate, pore and cracks in the particle, boundaries between cement paste and

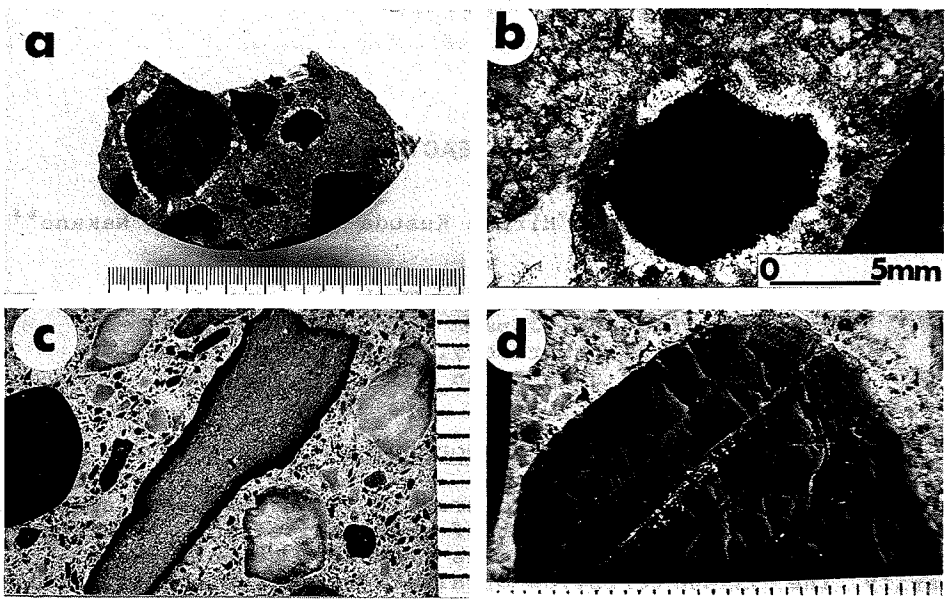

Photo 1. Products of the alkali-silica reaction in deteriorate concrete cores. a:A deteriorated concrete core(Sample Ch-16), b:Reaction products on the boundaries between chert particle and cement paste(Sample Ch-16-6), c:Dark rims in an alkali-reactive chert aggregate(Sample Ch-1-2), d:Reaction products in an alkali-reactive chert aggregate(Sample Ch-8-1).

particle, and outside of the particle.

Careful examination under a stereomicroscope and a polarizing microscope was performed on the thirty particles of alkali-reactive chert taken from deteriorated concrete. The additional signs of reactivity such as reaction products, dark rims, and fillings within three different parts of the particles were illustrated in several grades (Table 1).

3. X-RAY DIFFRACTION ANALYSIS (XDA) AND DIFFERENTIAL THERMAL ANALYSIS

The chemical reactivity of silica minerals with cement alkali has been discussed by many authors e.g.[3],[4] in terms of profiles of certain X-ray diffraction peaks or of differential thermal peaks. Representative silica minerals which have various degrees of crystallinity including chalcedony, agate, rock crystal etc., were analyzed by X-ray diffraction analysis (XDA) and differential thermal analysis (DTA). Particular attention was paid to two sets of five-peaks at 2θ ranges of 79° to 82° and 153° to 158°, $CoK\alpha$ radiation and endothermic peak at about 573℃. Poorly crystallized forms of silica exhibited X-ray diffraction patterns with markedly broadened peaks in the back-reflection region, and a very broad shallow endotherm with the profiles of differential thermal peaks.

The factors to determine semiquantitative methods of measur-

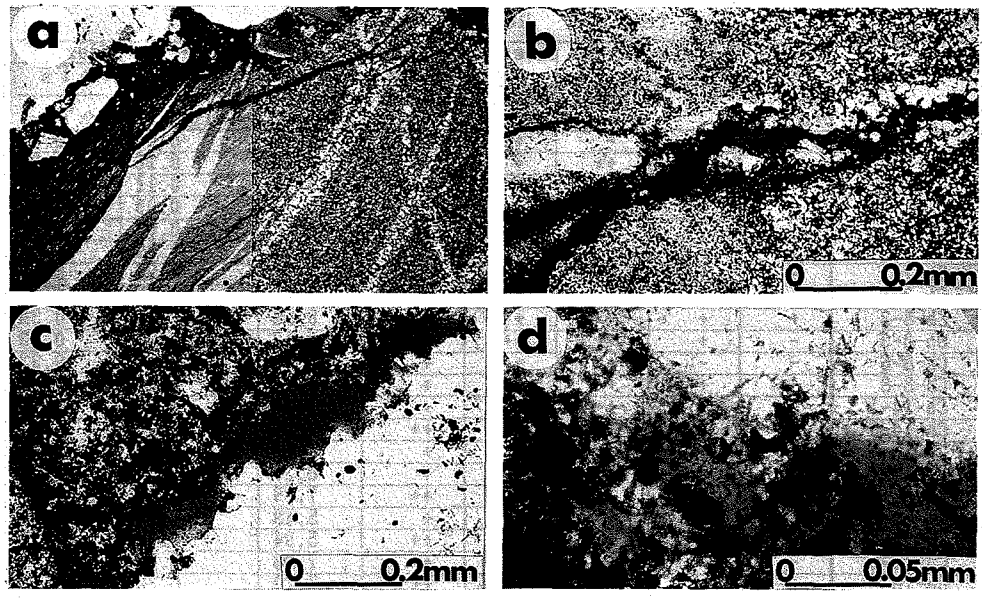

Photo 2 Products of the alkali-silica reaction on the boundaries between chert particle and cement paste and in the particle.
a:Fillings of irregular microcracks. (Half the photo on left hand side; open nicol, half the photo on right hand side; crossed nicols, sample Ch-16-7), b:Reaction products of irregular shapes in quartz vein.(Half the photo on left hand side; open nicol, half the photo on the right hand side; crossed nicols, sample Ch-16-1), c,d:Reaction products on the boundaries between chert particle and cement paste. Obscure boundaries illustrate dissolution of silica.(Open nicol, sample Ch-7-1 and Ch-8-1).

ing crystallinity are as follows.

(1) Crystallization index of a set of five peaks at a 2θ range of 79° to 82° , CoKα radiation.

The method of computing the crystallinity from the intensity of the (212) peak (Fig 2.a) has been made, adopting the method described by Murata and Norman (1976)[5]. Height (a) of the (212) perk is divided by its total height (b) above the background (Fig 2.a). The equation used is

$$\text{crystallization index} = 10 \cdot F \cdot a / b$$

F is a scaling factor to convert the maximum value (in this study, intensity of rock crystal) into 10.

(2) Crystallization index of a set of five peaks at 2θ range of 153° to 158° , CoKα radiation.

In general, the relative intensity pattern of the peaks of the qiuntuplet is shown in Fig 2.b. Height I_1 is the strongest intensity of (403) peak at 2θ of 155°. Among the better crystallized samples, an occasional pattern is obtained in which the peaks of I_2, I_3 and I_4 of them are stronger than poor crystalized samples(Fig. 1.b). The variation in the overall intensity

Table 1 Results obtained

	Observation under a stereomicroscope			Observation under a microscope		Crystallization index		
	Reaction products	Rim	Inside	Boundary	Outside	$10 \cdot F \cdot \frac{a}{b}$	$\frac{(I_2+I_3+I_4)_S}{(I_2+I_3+I_4)_{RG}}$	$\frac{\Delta T_S}{\Delta T_{RG}}$
Ch-3-1	++	+	-	++	++	2.12	0.04	0.08
Ch-6-1	-	-	++	+	+	4.48	0.16	0.37
Ch-6-2	-	++	+	+	+	3.43	0.11	0.24
Ch-6-3	-	-	++	++	+	5.17	0.09	0.14
Ch-7-1	-	-	+	++	+	2.50	0.08	0.14
Ch-7-2	+	-	-	+	-	4.96	0.09	0.37
Ch-7-3	-	+	-	-	-	6.88	0.59	0.45
Ch-8-1	-	-	++	++	++	2.16	0.09	0.24
Ch-8-2	+	+	-	+	+	6.58	0.36	0.35
Ch-8-3	-	+	++	++	+	5.17	0.09	0.33
Ch-8-6	-	-	+	+	+	3.69	0.19	0.33
Ch-8-8	-	+	+	+	+	5.74	0.18	0.53
Ch-14-1	-	+	++	++	+	2.84	0.08	0.14
Ch-14-3	-	+	++	++	++	6.14	0.29	0.69
Ch-15-1	-	-	++	+	+	8.49	0.76	0.78
Ch-15-2	-	-	+	+	+	8.27	0.77	0.69
Ch-16-1	++	+	++	+	++	7.29	0.63	0.71
Ch-16-3	-	+	+	+	+	5.49	0.33	0.33
Ch-16-4	-	+	-	++	++	5.94	0.18	0.53
Ch-16-5	-	-	+	+	+	7.88	0.83	0.69
Ch-16-6	++	+	-	+	++	7.10	0.20	0.61
Ch-16-7	+	-	+	+	+	7.50	0.63	0.65
Ch-17-1	-	+	-	++	++	6.09	0.23	0.37
Ch-17-2	+	+	+	++	++	5.94	0.16	0.45
Ch-17-6	-	+	+	+	++	7.74	0.48	0.57
Ch-17-7	-	+	+	+	+	6.85	0.48	0.69
Ch-17-8	-	+	++	+	+	4.69	0.09	0.25
Ch-19-1	-	+	-	++	++	7.09	0.58	0.71
Ch-19-3	-	-	-	-	+	5.58	0.18	0.73
Ch-19-6	-	+	-	+	++	5.72	0.07	0.18
rock crystal						10.00	1.00	1.00
hornfels						5.56	0.55	0.53
chalcedony						0.83	0.06	0.04
agate						0.83	0.00	0.02
jasper						0.39	0.00	0.06

++,+,- illustrating differences in sign of alkali-reactivity among samples.

of the pattern is measured by the ratio of the total height of I_2, I_3 and I_4 of sample to that of standard material(rock crystal).

The equation is

$$\text{crystallization index} = \frac{(I_2+I_3+I_4)\text{sample}}{(I_2+I_3+I_4)\text{standard}}$$

(3) Estimation of the crystallinity from DTA patterns.

Variation of the endothermic peak at about 573℃ is used to evaluate crystallinity of silica (Fig 2.c). The ΔT value of the peak of sample is compared with that of standard material (rock crystal).

The equation is simply

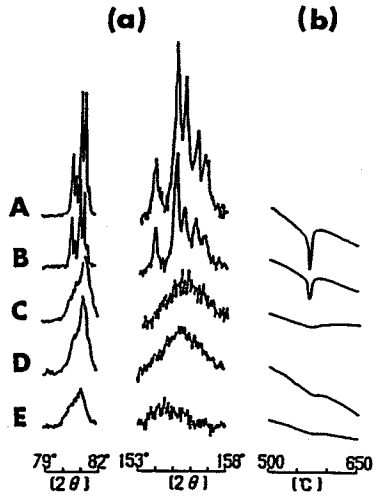

Fig.1 X-ray diffraction pattern (a) and Differential thermal pattern (b). A:rock crystal, B:hornfers, C:chalcedony, D:agate, E:jasper

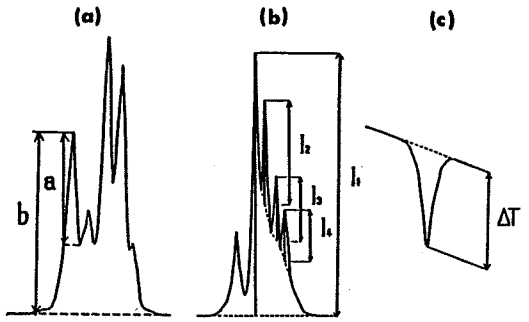

Fig.2 The diffractogram of rock crystal at 2θ of 79° to 82° (a) and 153° to 158° (b),and the endothermic peak of rock crystal at 573℃ (c)

$$\text{crystallization index} = \frac{\Delta T \text{ sample}}{\Delta T \text{ standard}}$$

Thirty chert particles and typical silica minerals were analyzed by a Nerelco X-ray diffraction with Fe filtered CoKα radiation and by a Shimadzu differential thermal analyzer. Results obtained are described in Table 1.

4. DISCUSSION

As already mentioned, these samples were collected from the various chert particles of nine deteriorated concrete cores. Figure 3 shouws the correlations among observations under a stereomicroscope and a polarizing microscope, and crystallization indexes from XDA patterns and DTA patterns. The microscopic findings of alkali-reactivity in terms of three grades, based on the total number of + mark of five items. Open square denotes remarkably reacted chert (total number of + marks is over 6); open triangle reacted chert (the total number is 4-5); and cross non-reacted chert (the total number is less than 3). All analytical values of the samples is in the range of low crystallinity such as chalchedony, agate and jasper into high crystallinity like such crystal. The crystallization index from X-ray diffraction patterns shows good agreement with that from DTA patterns (Fig.3.a,b). Remarkably reactive chert has relatively low crystallization indexes. Especially the value of crysindex obtained from five peaks at a 2θ range of 153° to 158° remarkably reactive chert particles except one sample is less than 0.3. A few non-reactive cherts show low crystallinities (Fig.3). It seems that these chert particles have not been alkali-silica

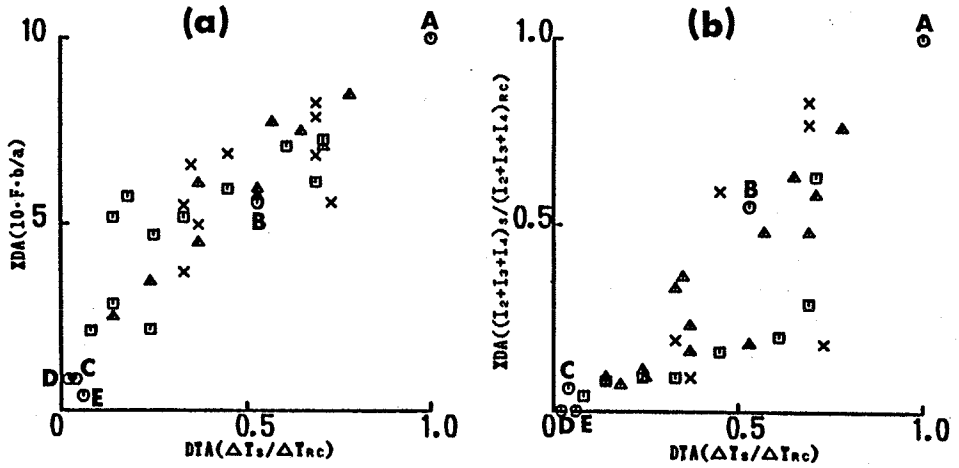

Fig.3 Correlations among observations under a stereomicroscope and a polarizing microscope, and crystallization index from XDA and DTA
□ :remarkably reacted chert under a microscope
△ :reacted chert under a microscope
× :non-reacted chert under a microscope
(A:rock crystal, B:hornfers, C:chalcedony, D:agate, E:jasper)

reactive due to reasons other than the characteristics of aggregate. These results confirm that the crystallization index from X-ray diffraction patterns is useful as a screening test for potential reactivity of chert.

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