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ALKALI AGGREGATE REACTIVITY OF CHERTY ROCK

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ABSTRACT

In this paper, alkali reactivity of cherty rocks was studied by methods of mineralogy or petrography together with concrete technology. Chert samples were collected from Mesozoic sedimentary formation in Yoro mountain and pit gravels in Aichi and Gifu prefectures, and chalcedony samples were selected from the laboratory collection. The properties of reactive minerals and rock-forming minerals in the samples were investigated with polarizing microscope, X-ray diffractometer and differential thermal analyzer. Chemical and expansion tests on the samples were carried out by chemical (ASTM C289 or JIS A 5308) and mortar bar (ASTM C227 or JIS A 5308) test methods.

Special attention was paid to the test results with regard to amorphous silica and crystallinity of quartz (cryptocrystalline and chalcedonic quartz) in chert. The relationship between the various results on microscopic properties of chert and the expansion behavior of mortar bar made with chert were presented.

1. INTRODUCTION

The damage to concrete due to alkali-aggregate reaction of chert has recently been discovered in several regions in Japan. Cherts are included in river and pit gravels and they are used in large quantities as concrete aggregate.

In this paper, alkali reactivity of cherty rocks is studied by methods of mineralogy or petrography together with concrete technology. Chert is a dense and very hard siliceous sedimentary rock composed of silica in the form of cryptocrystalline quartz, chalcedony, or opal, or combination of any of these three. Chert also shows a high degree of transparency and various colors. Even small amount of impurities such as iron, manganese, clay minerals and carbonaceous materials, cause a color change.

The classification of chert in Japan is based on two different criteria which are independent of each other [1]. According to the first criterion, chert is divided into opaline or quartzose based on the crystalline state of the main silica constituent. Opaline chert includes amorphous silica, opal-CT, low cristobalite and tridymite. By the second criterion, chert is classified into primary and secondary (or replacement) base of the origin of the main silica constituent. Primary chert originates as an aggregate of siliceous skeletons or as a chemical precipitate. The former is called biogenic chert; the latter, chemical chert. Secondary chert is produced by substitution of opalline silica, or quartz for non-siliceous sediments, for example, carbonate--replacement chert.

In Japan, radiolarian chert and siliceous shale are abundant in the Chichibu Tarrane deposited from Late Paleozoic to Mesozoic time. The Upper Triassic chert is the most widespread siliceous rocks in Japan. Jurassic radiolarian siliceous shale and bedded chert occur at some places, for example, Inuyama and Kuzuu. The Chichibu Tarrane and locations of the collected samples are shown in Fig.1.

2. EXPERIMENTAL METHOD

2.1 Materials

Chert samples are crushed stone, A, and two kinds of pit gravels, B and C. Chert crushed stone were collected from Mesozoic sedimentary formation in Yorou mountain. Pit gravels in Aichi and Gifu prefectures were collected from Tertiary deposits, which had the rock origin from Late Paleozoic to Mesozoic time. The color differences of the chert samples were determined visually and marked by suffix one to five. Number one is a mixed sample, two is white, three is black, four is red and five is green. Mineral samples such as chalcedony, agate, jaspar and euhedral quartz were selected from the labolatory collections.

Normal portland cement containing 0.65% alkali as equivalent Na_2O (Na_2O: 0.19, K_2O: 0.70 %) was used. Total alkali contents of the mortar were adjusted in the range from 0.8 to 1.5 % alkali as eq. Na_2O by the addition of NaOH reagent. Silica sand (Sc: 11.7 m mol/l, Rc: 27.0 m mol/l) was used as a non-reactive material.

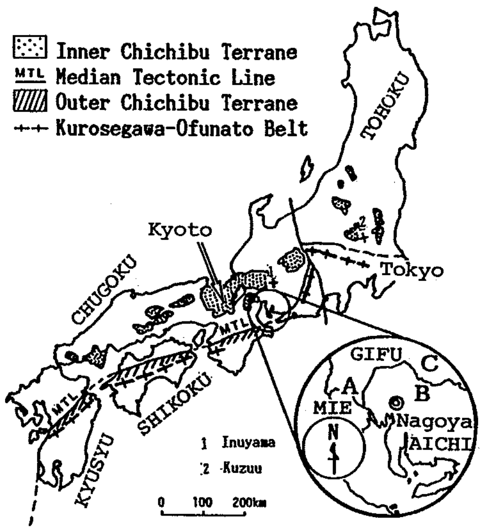

Fig. 1 Map showing The Chichibu Terrane and locations of the collected samples (Modified Iijima and Utada [1])

2.2 Test Methods

The petrographic properties of samples were tested by ASTM C295 Test Method(Petrographic examination of aggregates for concrete). The crystallinity of quartz was measured by X-ray diffraction using the method developed by Murata and Norman [2]. An index of crystallinity was derived from the intensity of the (212) peak at 2θ of 67.74°, CuKa radiation.

Potential reactivity of aggregates were tested by ASTM C289 Test Method or JIS A 5308 Test method(Chemical Method) and C227 Test Method or JIS A 5308 Test method(Mortar Bar Method). The size of mortar bar specimens made were 28x28x285 mm and 40x40x160mm.

3. RESULTS AND DISCUSSIONS

3.1 The Petrographic Characteristics of Chert Aggregates

The mineral compositions in chert aggregates were observed under polarizing microscope, and the typical results were shown in Table 1. The large amount of radiolarians fossils in cherts after etching with hydrofluoric acid were observed under scanning electron microscope. ASTM C289 chemical test results of these aggregates are also shown in table 1. Most of the aggregates are deleterious or potentially deleterious aggregates.

Table 1 Mineral compositions and ASTM chemical test results of chert aggregates

chert	chalcedony		cryptocrystal-line quartz	strained quartz	quartz vein		Rc (mmol/l)	Sc (mmol/l)	Sc/Rc	CI
	radial	banded			fine quartz	coarse quartz				
A 1 (Mix)	+++	+++	+++	±	+	±	88	391	4.44	5.01
A 2 (White)	+	+	++	±	++	+++	172	421	2.45	5.70
A 3 (Black)	+++	+++	+++	±	+	±	85	512	6.02	5.27
A 4 (Red)	+++	++	+++	±	+	+	83	149	1.80	4.32
A 5 (Green)	+++	+	+++	±	++	±	139	307	2.21	4.96
B 1 (Mix)	++	+	+++	+	+	++	58	116	2.00	7.14
B 2 (White)	+		++	+++	+	+++	42	110	2.62	6.56
B 3 (Black)	++	+	+++	+	±	+++	37	110	2.97	6.67
B 4 (Red)	+++	+	+++		++	+	52	113	2.17	5.96
B 5 (Green)	+++	+	+++	+	+	+	92	143	1.55	3.92
C 1 (Mix)	++	+	+++	+	+	++	95	107	1.13	6.81

amount of minerals +++>++>+>±

3.2 The Crystallinity of Quartz in Chert Aggregates and Chalcedonic Samples

The method of computing the crystallinity index from the intensity of the(212)peak at 67.74°, which is marked with an asterisk in Fig.2, is shown by means of a pattern of a well crystallized sample. Height a of this peak is first divided by its total height b above background in order to compensate for minor variations in the overall intensity of the pattern. The highest value (6.0) of quantity 10a/b was obtained most consistently with clear euhedral crystals of quartz, like the optical glass raw materials.

$$\text{Crystallinity Index (CI)} = \frac{10\,a\,F}{b}$$

$F = 1.62$

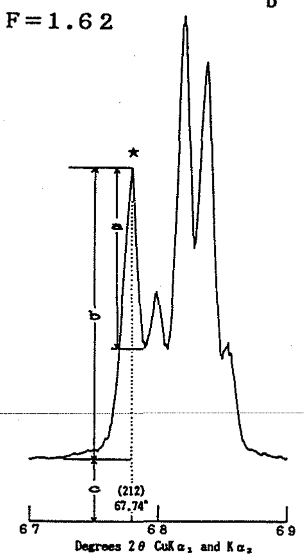

Fig. 2 The 68° quintuplet in the XRD of well crystallized quartz

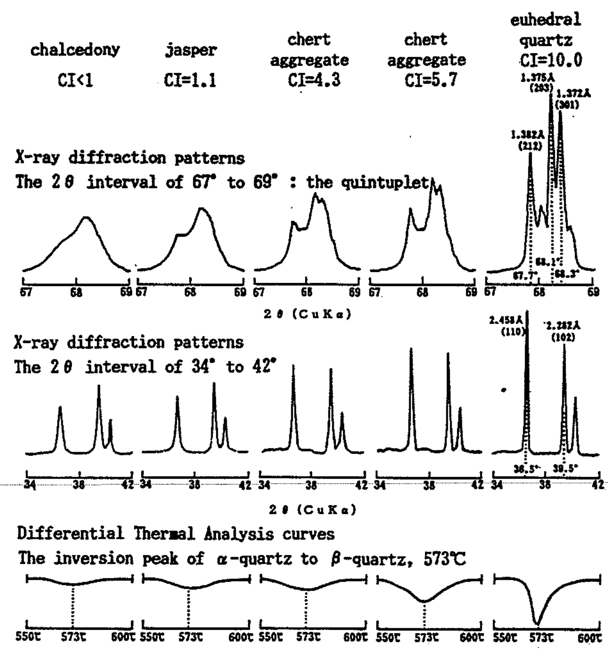

Fig. 3 Characteristics of XRD patterns and DTA curves of cherty rocks

In order to express crystallization indexes on the familiar scale of 10, the maximum determined value is raised from 6.0 to 10.0 by using a scaling factor F of 1.62. The scaling factor F would probably vary from one diffractometer to another. Fig.3 shows some typical examples of the results obtained from X-ray diffraction(XRD) and differential thermal analysis(DTA). There is a near quantitative connection between the crystallinity index (CI) of quartz and the DTA curves of high-low inversion. The relation between the strongest 3.343A (101)peak at 26.6° of quartz and CI of quartz are shown in Fig.4. An adequate correlation is estimated from a coefficient of correlation of 0.938.

3.3 The Relation between Crystallinity Index and ASTMC289 Chemical Test Result

The crystallity indexes of various samples were plotted on the illustration showing results of ASTM C289 chemical test, as shown in Fig. 5. An obvious relation is observed between crystallinity index and dissolved silica or between crystallinity index and reduction in alkalinity.

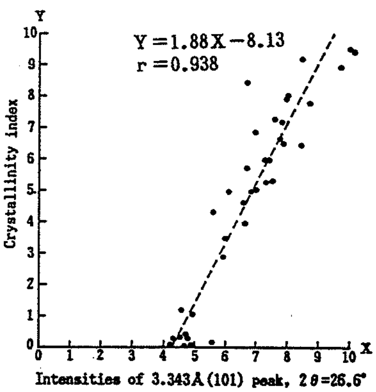

Fig. 4 The relation between crystallinity index and the strongest 3.343Å(101) peak of quartz

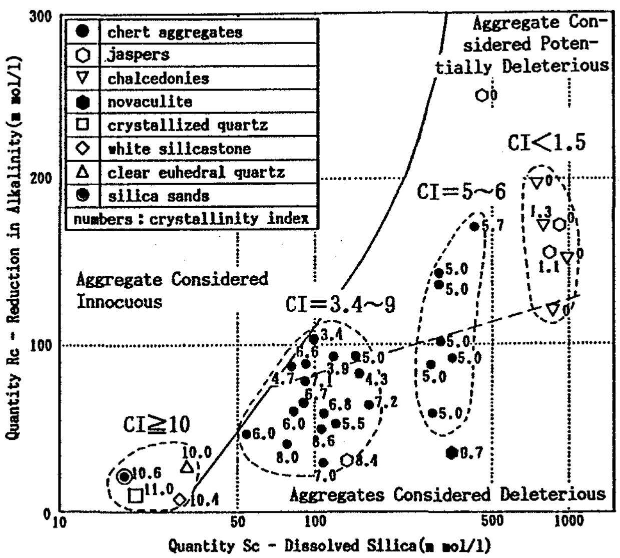

Fig. 5 The relation between ASTM C 289 chemical test results and crystallinity index of quartz

3.4 Expansion Behavior of Mortar Bar Made with Chert Aggregates

The expansion behavior of mortar made with various kinds of the colored cherts are shown in Fig.6 and Fig.7. It is difficult to find a certain relation between color of chert and expansion in these figures. As shown in Fig.7, the expansions of mortar bar of 0.8% alkali content as eq. Na_2O are small regardless of the mix proportions of chert and silica sands. The expansions of each aggregate become bigger, and pessimum phenomena can be clearly seen, when total alkali content is increased to 1.2% as eq. Na_2O. A2, A3, A4 and A5 aggregates were gathered at the same time from several pleces inside of chert crushed stone quarry A. However, there is a difference in expansion bahavior even in the cherts gathered this narrow area.

The relation between expansion of mortar bar and ratio of dissolved silica to reduction in alkalinity(Sc/Rc) is shown in Fig.8. An adequate correlation is estimated from the results. The correlation between expansion and crystallinity index of quartz is shown in Fig.9. From these figures, it became clear that the crystallinity index of quartz can be used as a rough standard for determining reactivity of cherty rock.

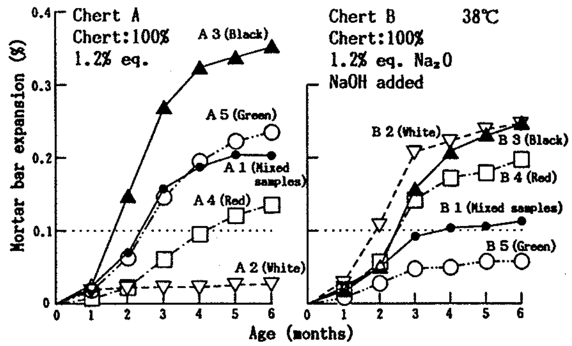

Fig. 6 The expansion of mortar bars made with various kinds of colored cherts

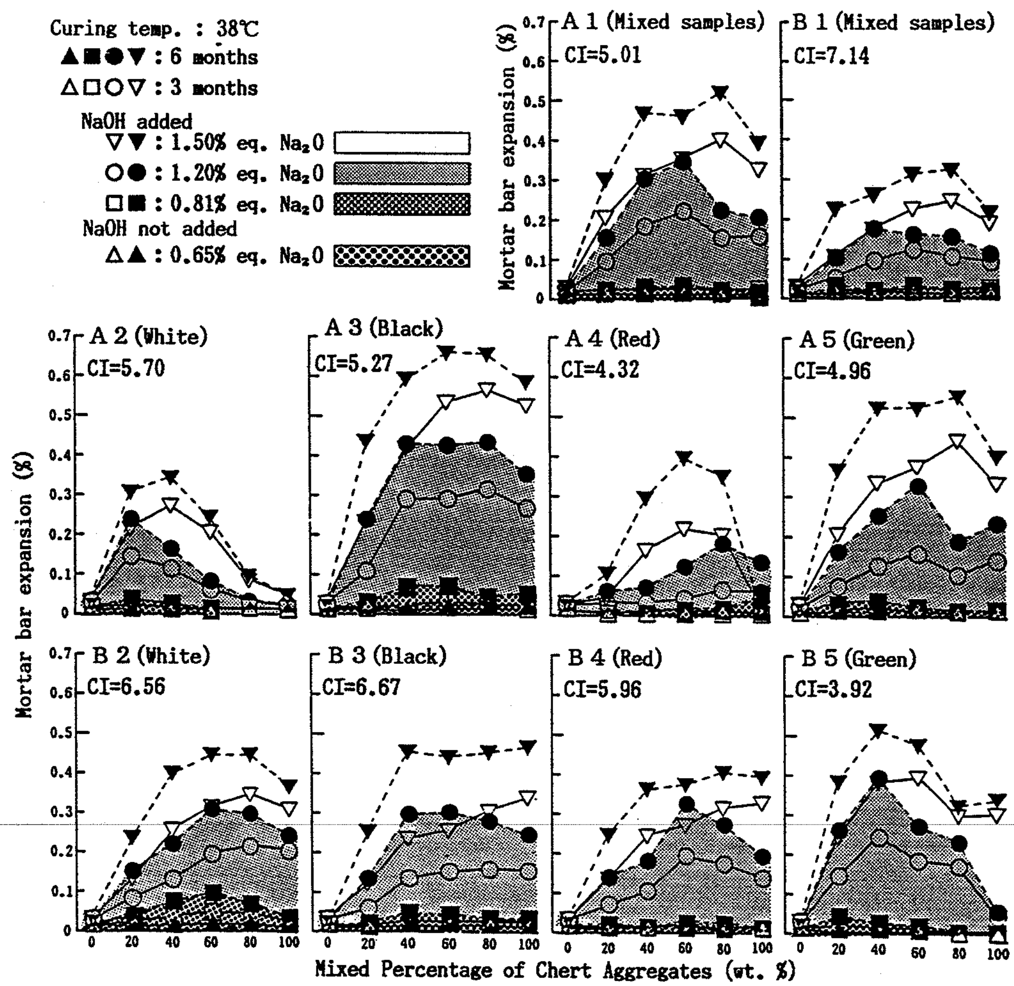

Fig. 7 The expansion behavior of mortar bars made with various proportion of chert and silica sands

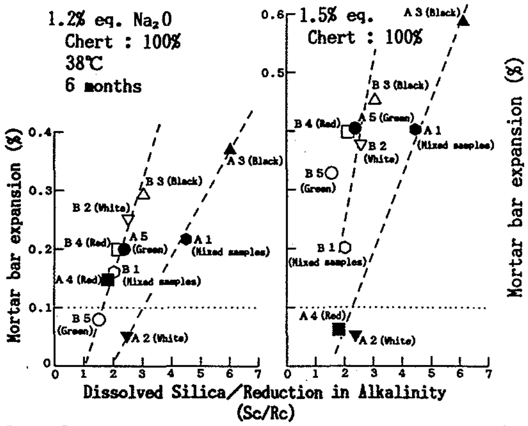

Fig. 8 The relation between expansion and Sc/Rc

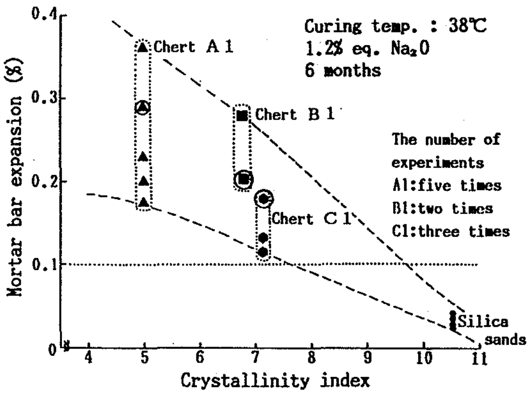

Fig. 9 The relation between expansion and crystallinity index

4. CONCLUSION

Results obtained are summarized as follows:

(1) The cherts used consisted largely of cryptocrystalline to microcrystalline quartz, with some chalcedony. Especially, the amount of the chalcedony showed a considerable variation with the types of cherts.

(2) The texture of chalcedony under polarizing microscope was radiating fibers. They were embedded in a matrix of apparently non-fibrous silica (opal). Under scanning electron microscope, chalcedony showed still a fibrous texture at low magnification, but appeared at high magnification as an assemblage of rod-like particles with uneven surfaces and of different sizes. The rod-like particles were seen clearly after etching with hydrofluoric acid, which preferentially dissolved a partial filling of opal(amorphous silica). Chalcedony were composed of chalcedonic quartz and opal.

(3) The XRD patterns of chalcedony were different in features from those of quartz : the 2.46A(110) peak of chalcedony was less intense and the 1.382A (212), 1.375A(203) and 1.372A(301) peaks were much less resolved than quartz. Such features of XRD patterns could be utilized to establish the presence of chalcedony in some cherts. An crystallinity index which was based on the degree of resolution of (212)peak, was taken as the presentative value.

(4) In DTA curves of chert, the high-low inversion of quartz(573 °C) were observed, and the shape of the inversion peak related to the amount of crystalline quartz in the sample.

(5) ASTM C289 chemical test revealed that cherts were deleterious or potentially deleterious aggregates, though mortar bars did not expand when normal portland cement of about 0.8% Na_2O equivalent was used. The expansion of mortar bar made with chert changed remarkably by the alkali content and mix proportion of non-reactive aggregate.

(6) There was a near connection between the crystallinity index and reactivity test results of cherts.

REFERENCES

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[2] Murata,K.J. and Norman, M.B., An Index of Crystallinity for Quartz, American Journal of Science, Vol.276, pp.1120-1130, 1976.