STUDY ON ALKALI CARBONATE ROCK REACTION OF JAPANESE LIMESTONE AGGREGATE

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ABSTRACT

The study was performed by petrographic examination (stereomicroscope, polarization microscope, SEM, EPMA) and expansion tests on concrete for the study of alkali carbonate rock reaction using limestone aggregates.

The results obtained are (1) Japanese dolomitic limestone shows rough texture of ore with higher crystallinity of carbonate ore as compared with Canadian dolomitic limestone. (2) Japanese limestone showed the expansion of concrete less than 0.01% in case of total alkali 3.1 and 5.5 kg/m^3. (3) By EPMA examination, Japanese limestone aggregate did not show any degeneration around the aggregate and remarkable reactive rim or movement of elements at the part of reactive layer.
Keywords: Alkali carbonate rock reaction, Expansion tests, Limestone aggregates, Petrographic examination.

INTRODUCTION

In Japan, there have been many cases using limestone as the aggregate for concrete. In the use of limestone as aggregate for concrete, an important problem is the reaction of alkali with carbonate rock which has been documented for a dolomitic limestone in Canada (CAN/CSA.1990).

This report is a summary of results of petrographic examination (X-ray diffraction, stereomicroscope, polarization microscope, scanning electron microscope (SEM) and electron probe micro analyzer (EPMA)) and concrete expansion test in the investigation and study of the types of limestone representative in Japan compared to the Canadian Pittsburg limestone which is recognized as an alkali carbonate reactive rock.

LIMESTONE AGGREGATE IN JAPAN

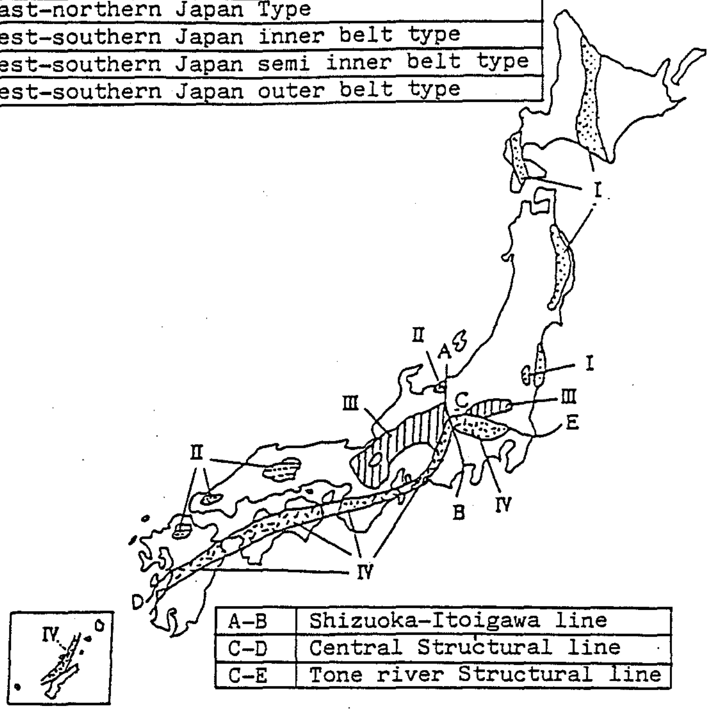
Limestone ore deposit

Japanese ore deposit of limestone belongs to that of Mesozoic era (triassic period, Jurassic period) and Paleozoic era (coal period, Permian period) (280 million-140 million years ago) and Cenozoic era 4 th period (1.5 million years ago).

Kawada (Kawada.1982) has classified the limestone ore deposit into 4 types as shown in Fig.1.

Type I is made of numerous big ore deposits as Japanese type ore deposit, and the layer-order is not distinct, also, the content of SiO_2 is a little more than the other types.

Symbol	Deposit
I	East-northern Japan Type
II	West-southern Japan inner belt type
III	West-southern Japan semi inner belt type
IV	West-southern Japan outer belt type



A–B	Shizuoka-Itoigawa line
C–D	Central Structural line
C–E	Tone river Structural line

Fig.1 Mesozonic and Paleozonic era layer deposit of limestone diagram

Type II is the ore deposit along the sea-side of the Sea of Japan of the central structural line. Geological age ranges from coal period to Permian period, and the content of CaO is rather high.

Type III means the ore deposit nearer to the central structural line than Type II. In geological age, it mostly belongs to Permian period, and in part to the coal period. The content of MgO might be a little more than the other types.

Type IV is distributed in Chichibu Zone on the side of the Pacific Ocean from the central structural line. Geological age ranges from coal period to Permian period, and partially ranges from Permian period to Jurassic period. The features on chemical ingredients are intermediate grades between Type II and III.

Selection of objective area for investigation and study

In Japan, limestone aggregate for concrete has been produced and shipped from 47 mines since 1993. Among them, 14 mines have been selected from all over Japan, to provide a balance of the area and type of ore deposit.

Table 1 shows the type of ore deposit selected and output as well as the shipped amount of aggregate for concrete (1993).

Table 1 The type of ore deposit selected and the output as well as the Shipped amount of aggregate for concrete

Mine name	Geological age	Type of ore deposit [1]	Location	Output (1,000t)	Limestone aggregate for concrete(1,000t)		
					Crushed stone	Crushed sand	Total
Garou		I	Hokkaido	5,560	1,300	200	1,500
Shiriya		I	Aomori Pref.	4,780	580	60	640
Hachinohe		I	Aomori Pref.	5,220	1,410	270	1,680
Nagaiwa	Mesozonic	I	Iwate Pref.	5,950	390	240	630
Ohganou	era	III	Ibaraki Pref.	270	30	-	30
Bukou	Paleozonic	IV	Saitama Pref.	4,660	1,040	360	1,400
Hikawa	era	IV	Tokyo Pref.	2,460	330	340	670
Fuziwara		III	Mie Pref.	4,470	850	-	850
Atetsu		II	Okayama Pref.	350	90	120	210
Isa		II	Yamaguchi Pref.	8,870	710	-	710
Sekinoyama		II	Fukuoka Pref.	5,060	890	420	1,310
Tsukumi		IV	Ohita Pref.	12,500	3,080	570	3,650
Torigatayama		IV	Kohchi Pref.	14,040	2,670	160	2,830
Anwa		IV [2]	Okinawa Pref.	2,520	1,190	-	1,190

*(1) Kawada. 1982.
(2) Miki. 1975.

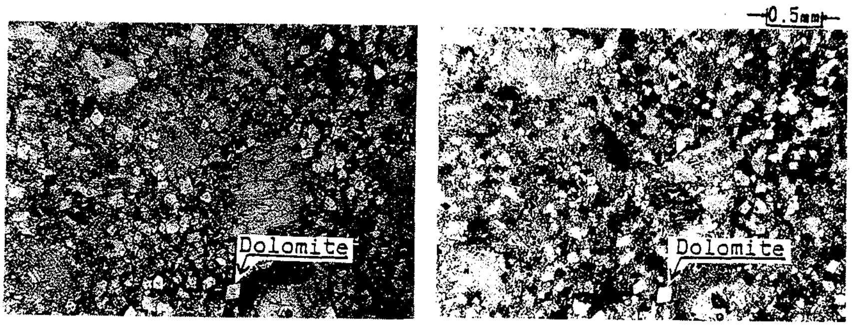
RESULT OF INVESTIGATION AND STUDY

Observation by polarization microscope

Figures 2-4 show the results of polarization microscope observation of Pittsburg aggregate produced in Canada and Type II produced in Japan (Ohganou and Hikawa aggregate) confirmed as dolomitic limestone.

From these figures, it is found that a character of dolomitic limestone produced in Japan exists as mosaic mass-body without showing the own form of dolomite (grain-shape: 100-200 μm), and the coexisting calcite is observed with rough granularity.

As compared with it, Canadian product showed the uniformly dispersed crystal (granularity: 20-60 μm) of dolomite in size of silt in the rock, and it is estimated that the fine granular mud rock of limestone containing big fossil might have been altered to dolomite.



Lower polar Crossed polar

Fig.2 Ohganou (Dolomite-type limestone)

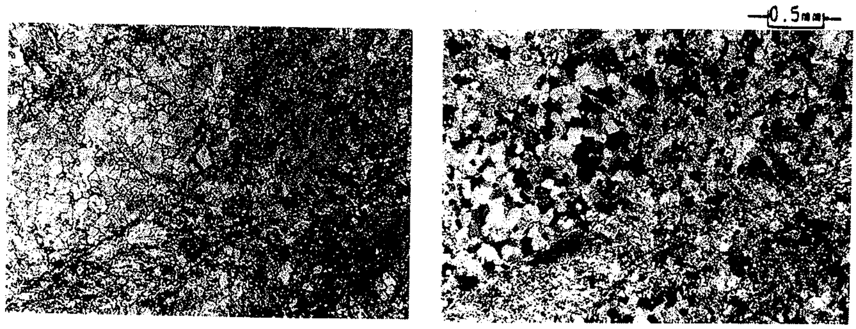


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Fig.3 Hikawa (Dolomite-type limestone)

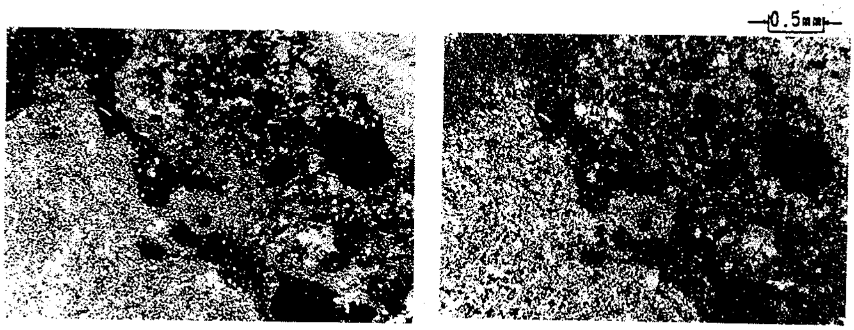

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Fig.4 Pittsburg (Dolomite-type limestone)

Result of X-ray diffraction analysis

Fig.5 shows a portion of X-ray diffraction diagram of Pittsburg aggregate produced in Canada and Japanese aggregate samples.

As a result, strong diffraction line of dolomite is observed in Ohganou aggregate and Pittsburg aggregate, and other types of aggregate showed slight diffraction line. Minor diffraction line of quartz was observed in Pittsburg aggregate. Diffraction line of calcite is observed in any aggregate.

TEST ON REACTIVITY OF ALKALI CARBONATE ROCK REACTION OF CONCRETE

Expansion test

Test has been performed in conformity with the CAN/CSA A 23.2-14A (concrete prism expansion test method).

The expansion was measured on 10x10x40 cm specimen, and the mix propotion of concrete shown in Table 2.

Cement was the ordinary portland cement with a total alkali content of 0.63% (equivalent of Na_2O), and the used fine aggregate was sea dredged sand with fineness modulus of 2.71.

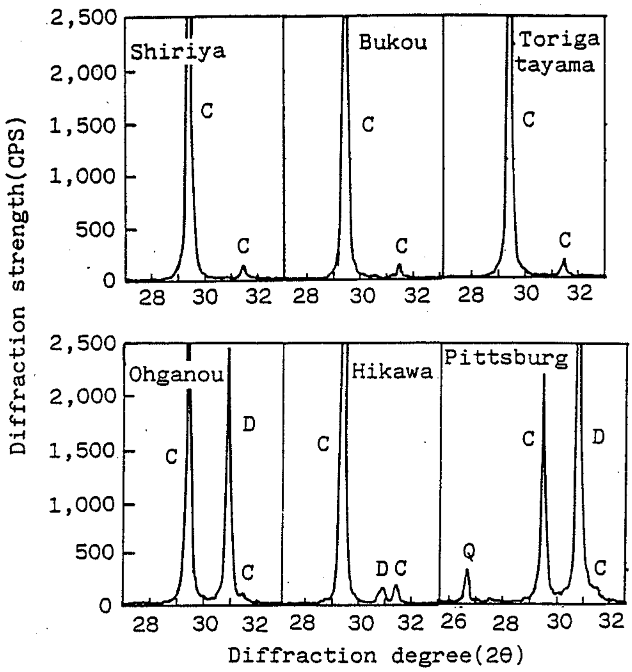

Fig.5 The diagram of X-ray diffraction of limestone aggregate samples (C:Calcite, D:Dolomite, Q:Quartz)

Table 2 Mix proportion of concrete

Water cement ratio (%)	Fine aggregate percentage (%)	Air content (%)	Unit weight(kg/m^3)			
			Water	Cement	Fine aggregate	Coarse aggregate
57	45	2.0	177	310	783	1031-1050

Total alkali content in concrete is specified to be 3.9 kg/m^3 expressed as equivalent Na_2O in CAN/CSA-standard. In this experiment, 2 levels have been used, namely, 3.1 kg/m^3 and 5.5 kg/m^3 as up/down of specified value. NaOH was used as adjusting agent of alkali content.

For measuring the expansion, specified age for material was set up to 168 days, and the judging standard expressed in CAN/CSA-standard (CAN/CSA.1990) for harmful expansion rate is set at over 0.04% regardless of the age. Fig.6 shows the result of the expansion measurements.

PITTSBURG AGGREGATE: At 14 days with 5.5 kg/m^3 and 28 days with 3.1 kg/m^3 of total alkali content in concrete, the expansion rate is already harmfully over 0.04%. At 168 days, concrete with 5.5 and 3.1 kg/m^3 show 0.33% and 0.20% expansion respectively, and expansion may be more later on so the Pittsburg aggregate is classified as alkali reactive as judged by the test criterion.

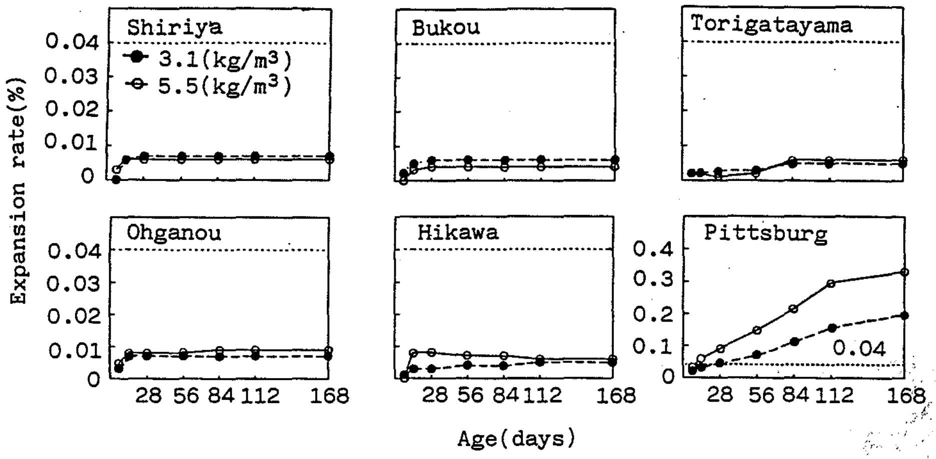

Fig.6 Variation of expansion rate versus time

JAPANESE LIMESTONE AGGREGATES AND DOLOMITIC LIMESTONE: All aggregates showed an expansion rate less than 0.01% even at 168 days, which is not harmful. Therefore Japanese aggregates are regarded as non reactive as judged by the test criterion.

Petrographic examination

A sample was collected from the concrete test specimens of total alkali content 5.5 kg/m^3 at 168 days.

For this sample, microscopic observation was made mainly on aggregate-cement paste interface.

By polarization microscopy of aggregate showing the reactive layer in Pittsburg aggregate, there is a distinct degenerated layer of aggregate observed in between aggregate periphery and paste (Fig.7). This means aggregate reacted. By SEM observation, the thickness of this reactive layer has been confirmed to be about 50 μm (Fig.8).

Moreover, by EPMA analysis in the aggregate side of the degenerated layer at the cement-aggregate interface (Fig.9), Ca and Mg concentration is reduced as compared with the central part of the aggregate, and Si concentration is elevated, also, Na and K concentrations are remarkably elevated.

The elements of Ca, Mg, Si, K are included in large quantity in the interior of Pittsburg aggregate.

Thus, the reactive layer might be formed by the movement of these elements. It is considered that the main component of these products was probably observed alkali-silicate, but alkali-silica gel was not observed. Japanese aggregate did not show any reacted layer around the aggregate. The movement of elements were not observed and the contents of Si, K were hardly observed from EPMA.

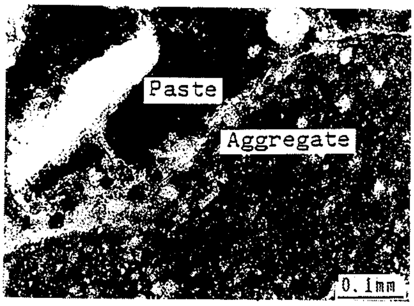

Fig.7 Polarization microscopic observation at the cement-aggregate interface of Pittsburg aggregate

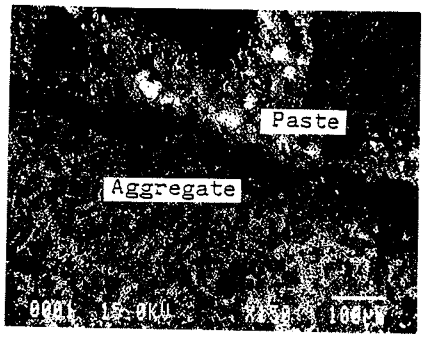

Fig.8 SEM observation at the cement-aggregate interface of Pittsburg aggregate

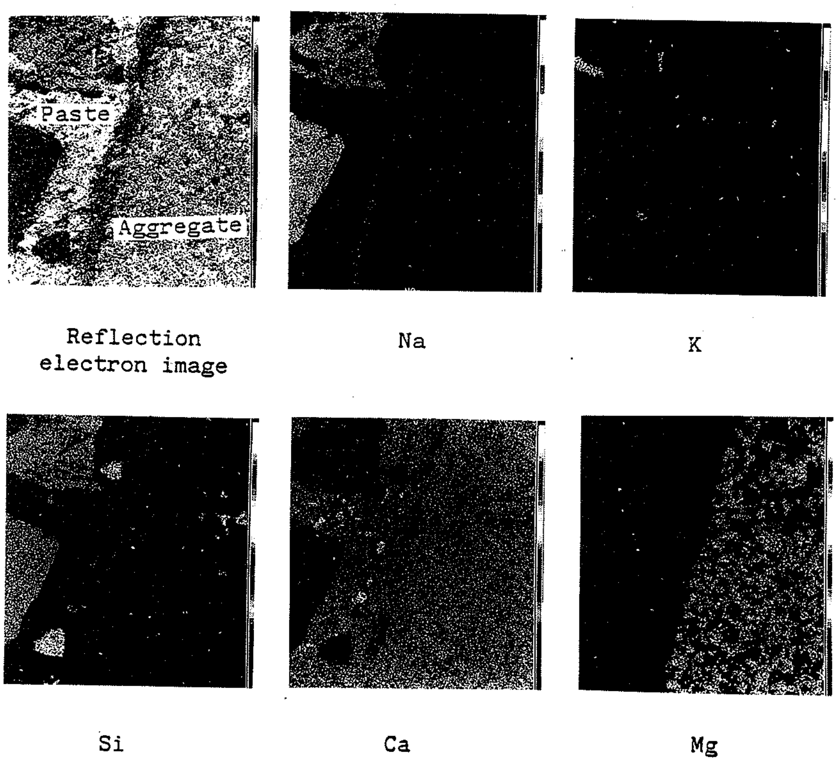

Fig.9 EPMA analysis by element of Pittsburg aggregate

CONCLUSION

Investigation has been made of the reaction of carbonate rocks with alkali for limestones used as aggregate for concrete. A comparison was made by using dolomitic limestone produced in Pittsburg of Canada, being an alkali reactive carbonate rock:

1) Japanese dolomitic limestone shows higher crystallinity of carbonate ore as compared with that in Canada, and ore texture is rough. Dolomitic limestone in Canada which is a fine and dense rock shows the uniformly dispersed fine crystals of dolomite in the matrix mainly with fine calcite.

2) Pittsburg limestone showed expansion of 0.20%, 0.33% for concrete with total alkali contents of 3.1, 5.5 kg/m^3. Whereas, Japanese limestone showed expansions rate less than 0.01%.

3) By EPMA examination, limestone produced in Pittsburg showed the movement of elements at reactive layer or degeneration around the aggregate and remarkable reaction rim. Japanese limestone did not show these remarkable phenomena.

As in the above, it was clarified that Japanese limestone showed no alkali carbonate rock reactivity.

REFERENCE

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