

## PROPOSAL OF A NEW INDEX FOR A MODIFIED CHEMICAL METHOD

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### 1. INTRODUCTION

Conventional evaluating methods for the aggregates to be used in concrete include Chemical Method and Mortar-bar Method. These methods merely determine the potential reactivity with an alkali and they are not effective for positive determination of whether a deleterious reaction occurs or not.

To effectively utilize the aggregates and to positively obtain a high durability concrete, an evaluating method which qualitatively tells the allowable amount of alkali in applying the aggregate to concrete is being sought.

The present paper reports on the results of reactivity tests for typical aggregates according to the existing Chemical Method, and outlines a newly proposed "Modified Chemical Method", which utilizes a new index indicative of the reactivity of the aggregate.

### 2. SEVERAL PROBLEMS IN CHEMICAL METHOD

The three-sectioned diagram used in the Chemical Method has been determined on the basis of numerous data obtained in the U.S.A. This standard, however, involves the following problems. First to be mentioned is the test condition employed in the course of determining the boundary line in the diagram, i.e., the Mortar-bar tests performed only with high alkali cement. Second to be noted is the use of extremely reactive aggregates containing highly alkali-reactive minerals.

Subsequent to the deterioration cases which happened in the U.S.A., similar cases were observed in Canada, Australia, and the West European countries, and the Chemical Method has come to be widely adopted as a rapid evaluating method. The boundary line drawn in the diagram is modified<sup>1, 2)</sup> so as to meet the type of aggregates characteristic in each country.

Also, in Japan, various examinations have been conducted, but the practical test still follows the ASTM-standard. The actual-state survey so far conducted by the present authors reveals that damages dominantly occurred on concrete structures using aggregates based on sedimentary rocks more often than with those based on volcanic rocks. Since Japan is complicated in its geological structure, the rocks to be used as aggregates widely range from volcanic to sedimentary.

Therefore, an evaluating method based on the ASTM-standard determined with aggregates having a high reaction rate would be unfit for universal application to the aggregates in Japan.

### 3. REACTIVITY OF TYPICAL AGGREGATES

#### 3.1 Aggregate Samples

Common aggregates are selected as the samples from among four volcanic rocks and six sedimentary rocks, ten in total. Mineral compositions determined by microscopic observation and X-ray diffraction technique are given in Table 1.

The table indicates that the main silica mineral responsible for the reaction with alkali is cristobalite in samples A1 and A2, volcanic glass in A3 and A4, and quartz in B1 to B6.

Among these minerals, quartz is further classified into chalcedony, cryptocrystalline, and microcrystalline, according to the crystallinity and grain size. The difference can be clearly observed from the fivefold lines in the X-ray diffraction pattern (Fig.1), or from the endothermic peak profile obtained by a differential thermal analysis (Fig.2), which is ascribed to the  $\alpha$ - $\beta$  phase transition of quartz. Samples B1 through B6 mainly consist of fine quartz, and apparently B1 partly comprises chalcedony.

#### 3.2 Experimental Procedure

Temporal changes of Sc and Rc, which are evaluating scales of the Chemical Method, are examined for every 12 hours over a period of 48 hours on typical aggregates of volcanic and sedimentary rocks for detailed investigation.

In order to perform a large number of test levels, the amount of the sample and that of the NaOH solution are selected 10g and 10cc, respectively, which correspond to 1/2.5 of the amounts employed in the Chemical Method. After treated, Sc is measured by atomic absorption spectroscopy, and Rc by titration with HCl solution.

Table 1 Mineral compositions of selected samples

Samples	Rocks	Feldpar	Quartz	Cristo.	Vol.g.	Mica	Others
A 1	Andesite	+++		++	+		Py., C.m.
A 2	Andesite	+++		++	(±)		Py.
A 3	Andesite	++	+	(±)	+++		Py.
A 4	Andesite	++		(±)	+++		Py.
B 1	Sandstone	++	+++			(±)	C.m.
B 2	Sandstone	++	+++			(±)	C.m.
B 3	Sandstone · Chert	++	+++			++	C.m.
B 4	Slate · Chert	+	+++			+	C.m.
B 5	Chert		++++				
B 6	Chert		++++			(±)	

(Cristo.:Cristobalite, Vol.g.:Volcanic glass, Py.:Pyroxene, C.m.:Clay mineral)

※) As quantitatively, +++++>++++>+++>+>(±)

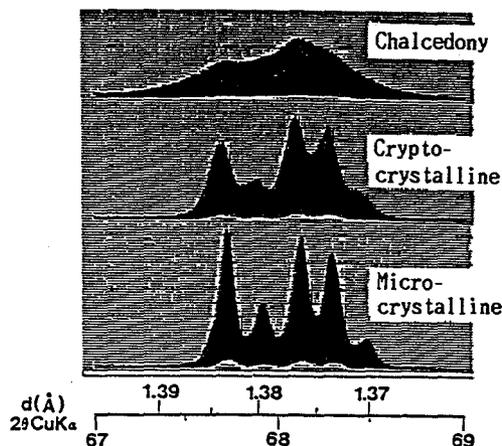


Fig.1 X-ray diffraction patterns of the fivefold lines of quartz

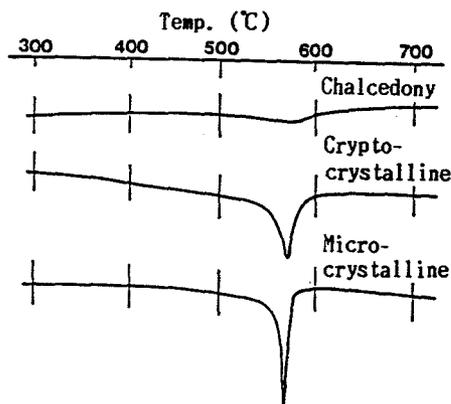


Fig.2 Endothermic peak profiles with the phase transition of quartz

### 3.3 Temporal Changes of Sc and Rc

Temporal changes of Sc for samples of volcanic and sedimentary rocks are shown in Figs.3 and 4, respectively. Sc in A1 to A4 increases rapidly at the initial stage of reaction (~12 hours), then, reaches a maximum and maintains the value. Though the time necessary to reach the saturation and the amount of Sc at the saturation vary with the type and the amount of silica mineral taking part in the reaction, the reactivity of cristobalite is extremely high as compared with that of volcanic glass.

On the other hand, Sc in B1 to B6 increases approximately linearly, and continues to increase even after 48 hours. This indicates that the reaction, in which cryptocrystalline quartz takes part, does not reach a saturation in the period of the present examination.

Temporal changes of Rc in samples of volcanic and sedimentary rocks are shown in Figs.5 and 6, respectively. The tendency in the change of Rc is, basically, in good accord with that of Sc. In particular, when cryptocrystalline quartz participates, the increase of Rc after 12 hours is in linear relation with the duration of alkali treatment.

### 3.4 Meanings of Chemical Method

It takes 24 hours for the final evaluation to be made in the Chemical Method. In the case of aggregates of volcanic rocks, this duration is enough or at least nearly enough to understand the reactivity. In the case of aggregates of sedimentary rocks, however, the reaction is still in progress and the potentially reactive amount cannot be precisely determined under the test condition. This signifies that the Chemical Method fails to consider the difference in reactivity depending on the silica minerals.

Thus, in the case of an aggregate containing cryptocrystalline quartz, underevaluation of the reactivity is likely to result. Particularly in the case of sedimentary rocks, one should be aware that the obtained value will not always be correct, since the reaction is still in progress.

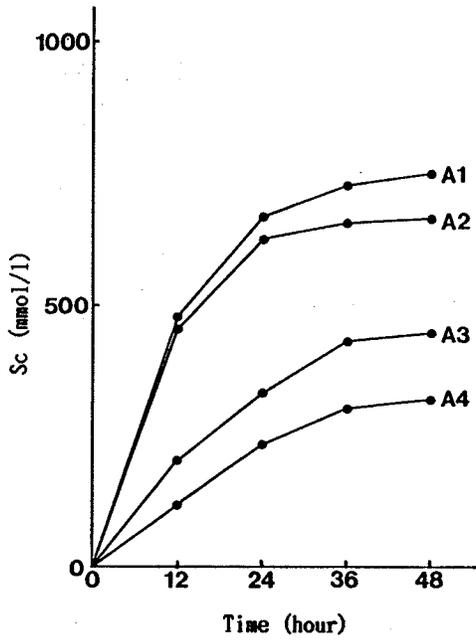


Fig.3 Temporal changes of Sc for samples of volcanic rocks

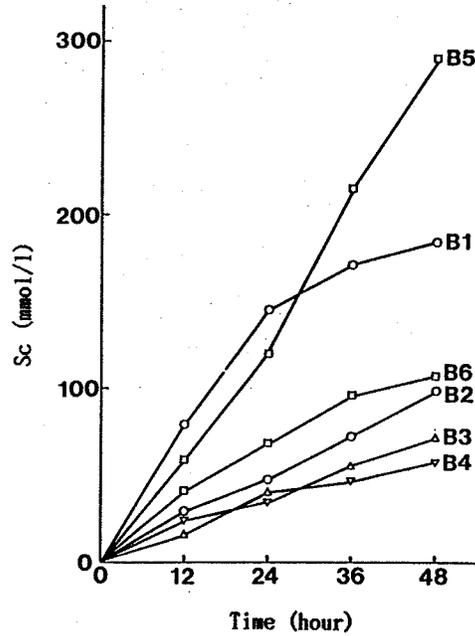


Fig.4 Temporal changes of Sc for samples of sedimentary rocks

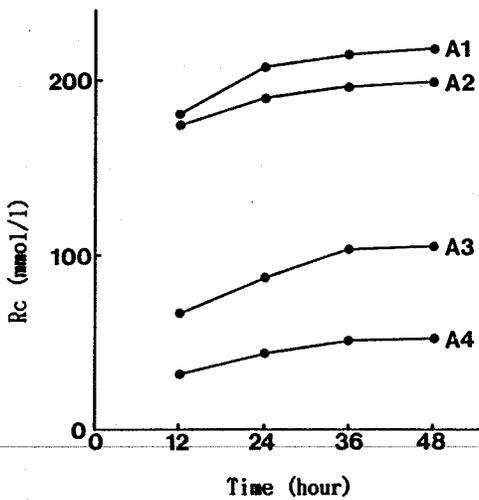


Fig.5 Temporal changes of Rc for samples of volcanic rocks

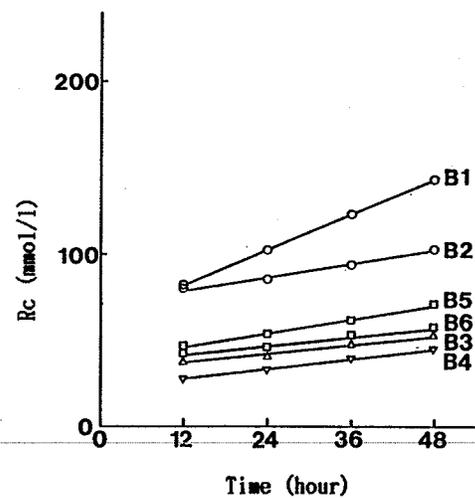


Fig.6 Temporal changes of Rc for samples of sedimentary rocks

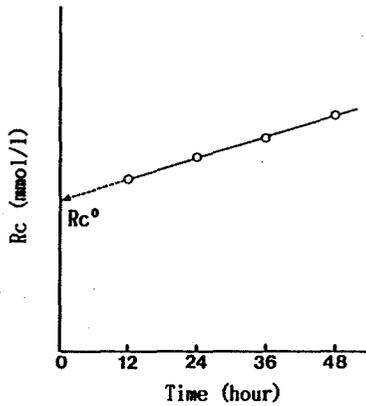


Fig. 7 Schematic diagram showing the way to obtain  $Rc^0$

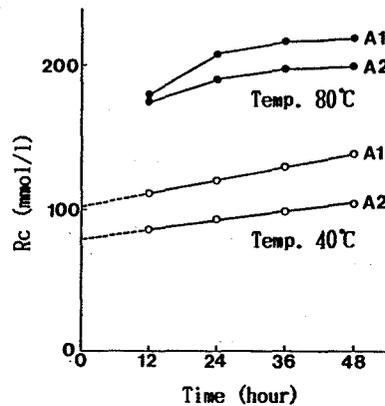


Fig. 8 Changes of  $Rc$  with the time varying the temperature

#### 4. PROPOSAL OF A NEW INDEX

Since  $Rc$  changes linearly as a function of time,  $Rc^0$  can be obtained by extrapolating the observed line on the  $Rc$ -axis, as shown in Fig. 7. This value is significant since each aggregate has a specific  $Rc^0$ , and it corresponds to "the alkali amount consumed for the reaction other than dissolution of silica mineral".

If this statement holds,  $Rc^0$  should be obtained for every kind of aggregate. In typical volcanic rocks such as A1 and A2, the changes of  $Rc$  show no linear relation with time. There are two approaches to making a linear approximation of  $Rc$  with time. One is to take a shorter time interval at early period, and the other is to delay the reaction itself. The former is prone to increase the experimental error, therefore, the latter is selected. Fig. 8 gives the result obtained with the temperature set at 40 °C. As evident from this figure, a decreased reaction rate enables a linear approximation of the change of  $Rc$  as a function of time, thereby yielding  $Rc^0$ .

In conclusion,  $Rc^0$  can be obtained, though there must be various measuring conditions according to the reaction rate of the aggregate, i.e., to the reactivity of silica mineral dominant in the reaction.

#### 5. PROPOSED EVALUATING METHOD FOR AGGREGATE BASED ON $Rc^0$

$Rc^0$  derived as a value characteristic of each aggregate was found to be closely related to alkali amount when concrete pieces showed no expansion. Based on the findings, the authors propose a "Modified Chemical Method" as shown in Fig. 9, to effectively estimate the allowable alkali amount in concrete.

According to this method, a reactivity test is first conducted to obtain  $Rc^0$ . In order to linearize the change in  $Rc$ , the test condition should be varied taking the reaction rate into account. Reactivity test I, to be held at 40°C, is selected for an aggregate having high reaction rate, and reactivity test II, to be held at 80°C, is the choice for an aggregate having low reaction rate. Since the alkali reactivity and  $Rc^0$  of an aggregate are obtained through the test described above, the allowable alkali amount is estimated with reference to expansion test data of concrete pieces using typical aggregates.

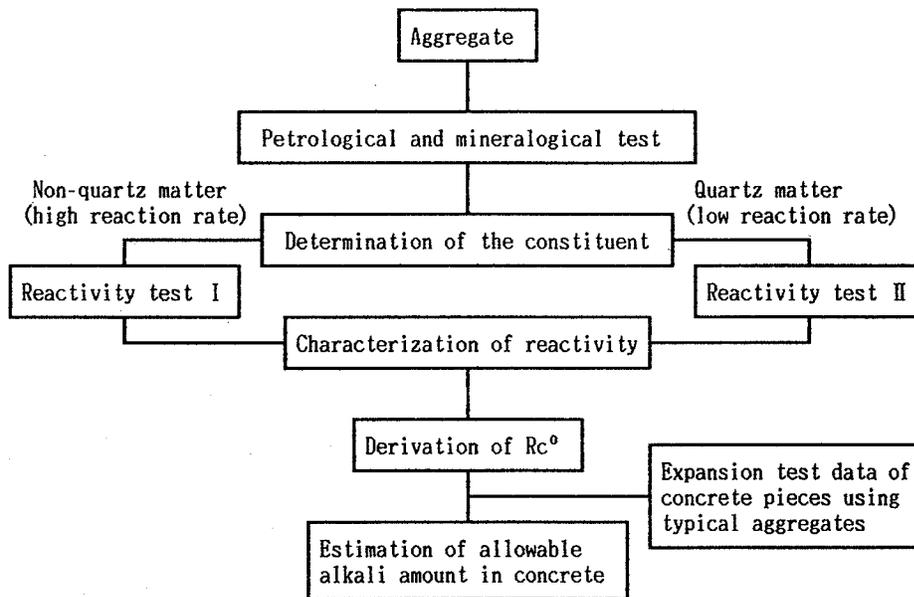


Fig.9 Modified Chemical Method

## 6. CONCLUSIONS

The Chemical Method, known as a useful method because of its rapidity, is modified by incorporating a new index  $Rc^{\circ}$ , a value characteristic of each aggregate. This "Modified Chemical Method" is proposed as a new evaluating method which enables the estimation of allowable alkali amount in concrete.

This method is advantageous in two points: an aggregate once rejected as being deleterious in the existing method may be evaluated and utilized in the ordinary cement; and the possible concrete deterioration due to underevaluation of reactivity, can be avoided. As a result, concrete improved in quality can be obtained with high durability, but one should bear in mind that this is only realized under a strict quality control of cement and aggregate.

## 7. ACKNOWLEDGEMENT

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