

EXPANSION PROPERTIES OF MORTARS AND VARIATION IN COMPONENTS  
OF PORE SOLUTIONS DUE TO ALKALI-AGGREGATE REACTION

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1. INTRODUCTION

It has been found that the expansion properties of mortar due to the progress of alkali-silica reaction had close relationships with alkali ions and hydroxide ions in pore solutions in mortars.

Pioneering researches on the relation between the expansion behavior of mortars due to alkali-silica reaction and concentrations of alkali ions and hydroxide ions in pore solutions were carried out by Diamond et al. [1]. As these studies were aimed to investigate the deterioration mechanism of cement materials due to alkali-silica reaction, the mortar specimens used for measurements of expansion and expression of pore solutions were all sealed in containers of synthetic rubber. Therefore both water and air could not move in and out.

The Mortar-Bar Method specified in ASTM C 227 and the method specified in JIS A 5308 are widely used as accelerated testing methods for judging alkali reactivity of aggregates by measuring expansion of mortar specimens. In these methods, specimens are stored in a high-humidity environment of 100% RH. to accelerate alkali-silica reaction.

When specimens are kept in this environment, they are subjected to penetration of water and carbon dioxide from outside. Under this condition, it is natural that concentrations of alkali ions and hydroxide ions in pore solutions and their time-dependent changes are different from the results obtained from specimens in sealed conditions.

This study contains the investigated result of expansion properties of mortar specimens and the investigated result of concentrations of alkali ions and hydroxide ions in pore solutions expressed from the specimens which were stored in the same environment as in the Mortar-Bar Method, and describes the relationship between the expansion and the concentration.

2. EXPERIMENTAL

Mix proportions of mortars had water-cement ratio of three levels of 0.40, 0.50, and 0.60, while unit water content was the same  $300 \text{ kg/m}^3$  in all mix proportions. Alkali in cement was varied at the three levels of 0.83, 1.04, and 1.56% in terms of  $\text{Na}_2\text{O}$  equivalent by addition of  $\text{NaOH}$  to ordinary portland cement of  $R_2\text{O} = 0.52\%$ .

Two reactive rocks and one non-reactive rock were used as aggregates. The reactive rocks were a glassy andesite judged as "potentially deleterious" and a chert judged as "deleterious" as a result of testing according to ASTM C 289.

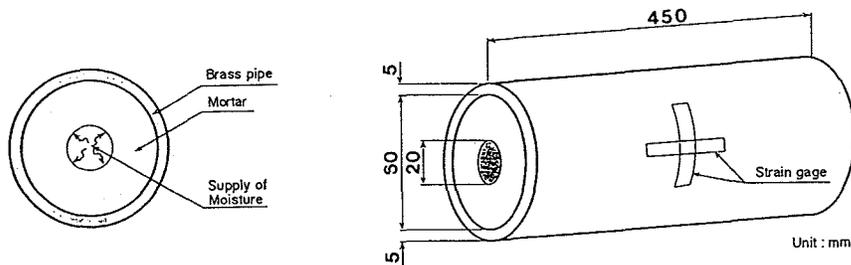


Fig.1 Specimen for measurement of restrained expression

The former contained approximately 40% of volcanic glass, and the latter contained approximately 90% of cryptocrystalline quartz. Limestone was used as the non-reactive rock.

Each batch of mortar mixed was divided into two parts with one cast in  $\phi 5 \times 10$ cm cylindrical molds and used for expressing pore solutions, while other was used to fill brass pipes of the dimensions shown in Fig.1 leaving the center portions hollow. The reason why hollow portions were left was to facilitate supply of moisture to the mortars.

These specimens, after holding in an environment of 20°C and 100% RH. for 24 hours after casting, were moved to an environment of 40°C, 100% RH.. And they were used either for measurement of restrained expansion or for expression of pore solutions. Some of the specimens for pore solution expression in which limestone and chert were used as aggregates were stored in sealed condition.

Restrained expansion, as shown in Fig.1, was determined measuring strains in the axial and circumferential directions using electric resistance wire strain gages, with expansion pressure(P) calculated applying the thick-shell cylinder equation given below.

$$P = \frac{(e_t + \nu e_z)E}{1 - \nu^2} \left\{ \frac{t}{r + t^2 / (2r^2)} \right\}$$

where  $e_t$  : strain in circumferential direction at surface of pipe  
 $e_z$  : strain in axial direction at surface of pipe  
 $E$  : Young's modulus of pipe material  
 $\nu$  : Poisson's ratio of pipe material  
 $t$  : thickness of pipe  
 $2r$  : inside diameter of pipe

Expression of pore solutions was carried out using high-pressure device developed by Longuet[2] and made practical by Diamond[3] and Page[4].

Analyses of alkali ions in pore solutions were performed by the atomic absorption spectrometry and analysis of calcium ion by flame photometry. Analysis of hydroxide ion was carried out by the titration with hydrochloric acid using phenolphthalein as an indicator.

### 3. RESULTS AND DISCUSSION

#### 3.1 Composition of Pore Solutions and Its Time-Dependent Changes

An example of the analysis results for pore solutions of mortars using andesite as aggregate is shown in Table 1. In this table, the composition of pore solutions expressed from specimens stored in a high-humidity environment such as specified in the Mortar-Bar Method is almost the same as the pore

solutions expressed from specimens in sealed conditions, and it can be seen that the greater part of the composition consists of alkali ions and hydroxide ions.

However this table also shows that the concentration of these, unlike cases of pore solutions expressed from specimens in sealed condition, decrease rapidly with the passage of time. As causes of this, dilution by supply of water from the outside, progress of carbonation, and distribution of alkali ions concentration at specimen interior are conceivable.

Fig.2 shows the time-dependent changes in alkali ion ( $\text{Na}^+\text{+K}^+$ ) concentrations in pore solutions expressed from mortars using chert and limestone as aggregates, and indicates, in the cases of storage periods 7 and 28 days, the values which were obtained from pore solutions expressed from specimens stored in sealed conditions for reference.

This figure shows that the concentrations of alkali ions decrease with time as the same result shown in Fig.1, and also that there is a distinct difference between the cases of using non-reactive aggregate limestone and the case of using reactive aggregate chert. And it can be seen that the decrease for the latter is prominent.

Table 1  
Analyses of pore solution expressed from mortars using reactive aggregate (andesite)

Time (Weeks)	Concentration(mol/l)					pH
	$\text{Ca}^{2+}$	$\text{Na}^+$	$\text{K}^+$	$\text{Na}^+\text{+K}^+$	$\text{OH}^-$	
1	0.0021	0.2610	0.0644	0.3254	0.3160	13.50
4	0.0043	0.1440	0.0309	0.1749	0.1820	13.26
13	0.0003	0.0843	0.0169	0.1012	0.0902	12.96
26	0.0004	0.0579	0.0113	0.0692	0.0494	12.69

\*  $R_2\text{O}=1.04\%$ ,  $\text{W/C}=50\%$

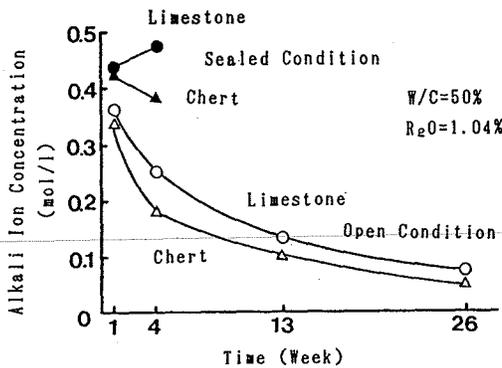


Fig.2 Time-dependent changes in alkali ion concentrations in pore solutions expressed from mortars

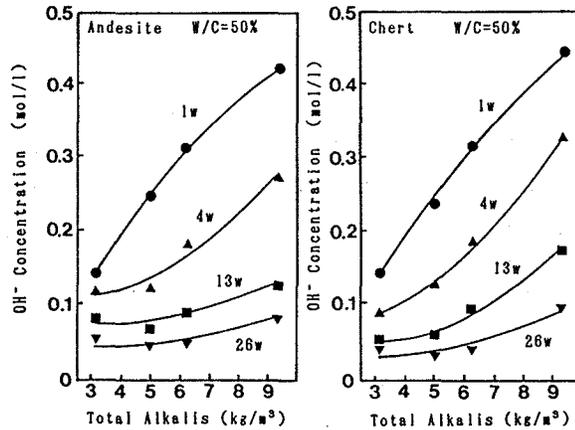


Fig.3 Relationships between total alkalis and OH<sup>-</sup> concentrations

The reason of this is thought as follows. In case of using chert as aggregate, the concentrations in pore solutions decreased because alkali ions were consumed by the progress of alkali-silica reaction.

Fig.3 shows the relationships between total alkalis in mortars using reactive rocks (andesite and chert) as aggregates and the concentrations of hydroxide ions in pore solutions.

It can be seen from this figure that whichever the aggregate used, the concentration of hydroxide ions in the pore solutions after a length of time has elapsed from the time of mixing depends on the total alkalis that were contained at the time when mixing was done.

As for the concentration of hydroxide ions, it shows a trend of converging to a certain given value as time elapses regardless of the total alkali quantity and variety of reactive aggregate, and this value in terms of pH is 12.6.

### 3.2 Relationship between the Composition of Pore Solutions and the Expansion Pressure

Fig.4 shows a comparison of the time-dependent changes in expansion pressures and the consumption of alkali ions concentration in pore solutions due to alkali-silica reaction of specimens using reactive rocks (andesite and chert) as aggregates. In this figure, it can be recognized that expansion pressure is comparatively low at an early age, but later increases gradually, and even at the 6-month age it is still increasing. In contrast, consumption of alkali ions reaches a maximum at an age of 1 or 4 weeks.

The time-dependent change in consumption of alkali ions is thought to indicate the Stage(I) in the proposal of Diamond et al.[1] concerning the deterioration process of concrete due to alkali-silica reaction, while the time-dependent change in expansion pressure indicates Stage(II). Diamond et al. basing on experiments, ascertained that the former precedes the latter, and it can be said that the trend shown in Fig.4 substantiates their thinking.

Fig.5 shows the relationships between a reduction in the concentration of alkali ions in pore solutions and expansion pressure. The values of concentration was determined by subtracting the alkali ion concentration obtained by analysis from the alkali ion concentration determined assuming that 1) all alkalis in cement are water soluble, and 2) all water-soluble alkalis are dissolved in mixing water.

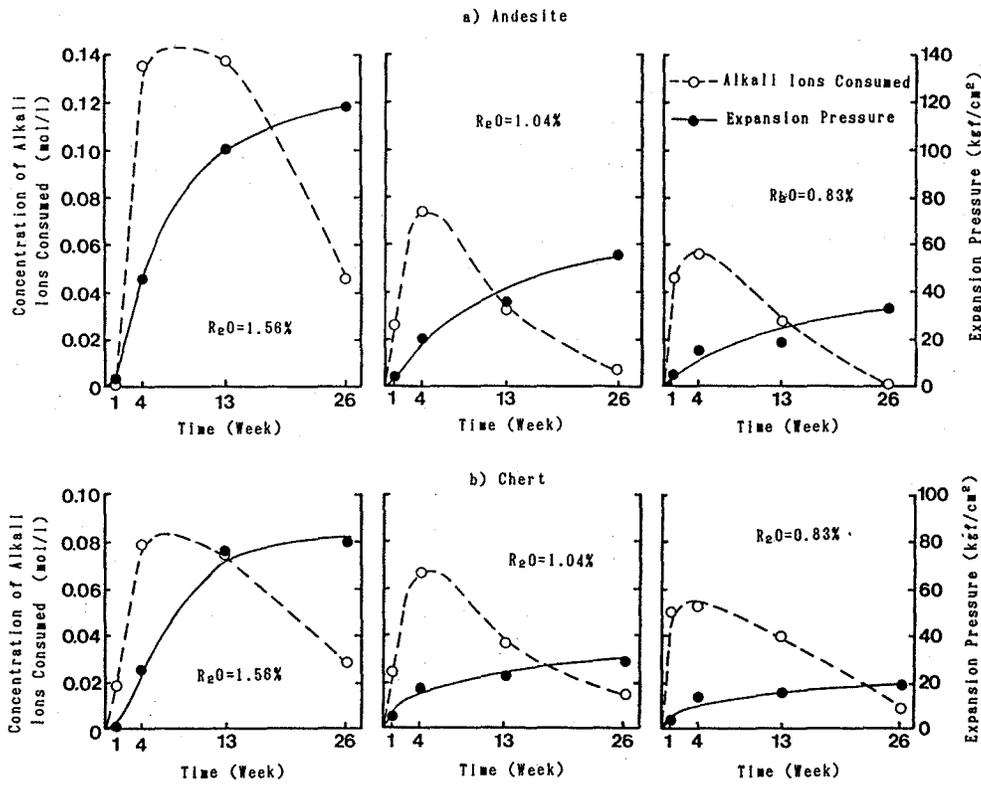


Fig.4 Time-dependent changes in consumption of alkali ions in pore solutions and expansion pressure

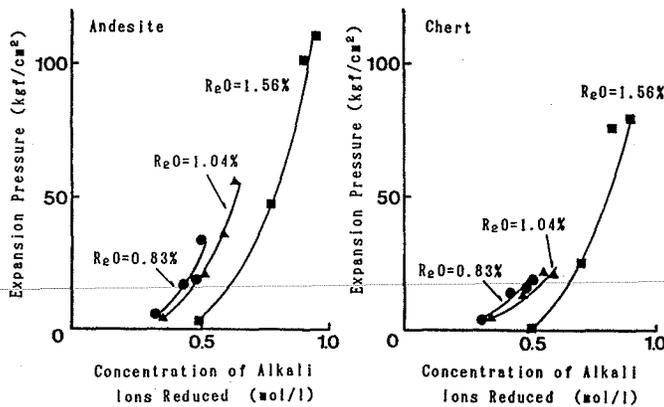


Fig.5 Relationships between reduction in concentration of alkali ions in pore solutions and expansion pressure

This figure shows that whichever reactive aggregate is used, expansion pressure increases as the amount of concentration reduction increases, that the reduction in alkali ions increases more the larger the total alkali content, and that the amounts of expansion differ depending upon the reactive aggregate even when the reduction in concentration of alkali ions are same.

It is thought that the reduction in concentration of alkali ions is mainly due to consumption of alkali ions following progress of alkali-silica reaction and the dilution by water taken in gel through absorption being wrung out when expressing of pore solutions is carried out. But in any case, the reduction in concentration of alkali ions in pore solutions will be one measure for estimating the alkali reactivity of aggregate and the degree of expansion.

#### 4. CONCLUSIONS

The composition of pore solutions expressed from mortar specimens stored in a high-humidity environment which is similar to the conditions of accelerated test such as the Mortar-Bar Method, is almost the same composition as for the specimens stored in a sealed condition.

This composition consists of alkali ions and hydroxide ions, but these concentrations were different from the case of specimens stored in sealed conditions. And these concentrations rapidly decreased with the passage of time. However, the pH of pore solutions did not decrease less than 12 even at 6-month age.

The concentrations of alkali ions and hydroxide ions in pore solutions showed good correlations with expansion, and the reduction in concentration of alkali ions would be useful as a measure for estimating the alkali reactivity of aggregate and the degree of expansion.

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