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A SIMPLE KINETICS BASED MODEL FOR PREDICTING ALKALI-SILICA REACTION

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An attempt has been made to present a new model based on kinetics that can predict the expansion behaviors of mortar bars. The model incorporates the effect of factors such as size and reactivity of aggregates, alkalinity of the cement matrix, etc.,

In this work, at first, change of soluble silica content and alkali-silica ratio of reaction products with the passage of time are measured by a leaching test. The results obtained are then analyzed on the basis of kinetics in order to obtain alkali diffusion coefficients in aggregates. The expansion behaviors can be calculated by using these diffusion coefficient and alkali-silica ratio of reaction products.

It is found that good agreement is observed in comparing the observed expansion behaviors with the calculated expansion behaviors in this way. Therefore, evaluating reactivity of the aggregates by using the model proposed here is useful to judge reactivity of aggregates quantitatively in short time.

1. INTRODUCTION

Alkali-silica reaction (ASR) has been identified as one of main causes for premature deterioration of concrete structures, and many papers have been published dealing with various aspects of the mechanism and its effect. In order to prevent deterioration due to ASR , it is important to evaluate the reactivity of aggregates before they are used. The mortar bar test defined as ASTM C 289 is the only quantitative method that can evaluate the reactivity of aggregates with physical value observed as expansion. However, the mortar bar test is time consuming, in particular, to obtain the ultimate expansion ratio which can be considered as indicating the potential reactivity of the aggregate.

In this paper, a simple kinetics based model is proposed to predict the expansion behaviors including the ultimate expansion ratio of mortar bars in short time. The model incorporates the effect of factors such as size and reactivity of aggregates, alkalinity of the cement matrix, etc.,

2. PROPOSED MODEL

2.1 Model to Approximate the Progress of ASR

ASR is considered as occurring in stages. Assuming that the rate-determining stage of ASR is diffusion of alkali ions from surface into the reactive aggregate, and that the alkali diffusion stage can be explained by a conventional diffusion theory, the following equation is derived from Fick's first law to approximate the extent of ASR as shown in Figure 1.

$$dt / dx = k\, C / x \qquad (1)$$

where, t, x, k and C represent time (hr), thickness of reacted layer (cm), diffusion coefficient of alkali ions in reactive aggregate (cm^2/hr), and alkali concentration in pore water of cement matrix (mol/l), respectively.

Since the alkali concentration in pore water, C, reduces with the progress of ASR, value of C has to be expressed as a function of x and alkali-silica ratio of reaction products (RS) which is considered as an important factor in determining alkali consumption efficiency in mortar bars.

$$C = f(x, RS) \qquad (2)$$

As can be seen from the inter-relationship between the equations (1)and (2), the model is a non-linear model consisting of equations (1) and (2) to calculate the thickness of the reacted layer from surface of aggregate particle.

Furthermore, assuming a spherical aggregate of radius R (cm), volume reaction ratio (α) of the aggregate particle with radius R can be written as

$$\alpha = 1-(1-x/R)^3 \qquad (3)$$

In this model, following unknown values are found.

k : diffusion coefficient of alkali ions in reactive aggregate (cm^2/hr)
RS : alkali-silica ratio of reaction products

Both analytical way and experimental way are conceivable to define these unknown values. In this work, values k and RS are obtained in experimental and analytical manner. A leaching test with the passage of time in accordance with the quick chemical method defined as ASTM C 289 is performed to obtain k and RS. The quick chemical method can only qualitatively show the reactivity of aggregates. However, a good correlation between the evaluations of chemical method and mortar bar method has been observed, and this indicates that the results from the chemical test can predict at least the expansion ratio of mortar bars at 6 months in a semi-quantitative manner. Therefore, the expansion behaviors can be predicted more quantitatively by analyzing the results from the leaching test with the passage of time on the basis of the model proposed here.

Following equation can be obtained by integrating equation (1).

$$x = \sqrt{2kCt} \qquad (4)$$

Since change of soluble silica contents of aggregate and the amount of consumed alkali with the passage of time are measured by the leaching test, alkali ion concentration C and alkali-silica ratio of reaction products (RS) are obtained directly. Thickness of the reacted layer x is also obtained by the following equation derived from equation (3).

$$x = R(1-(1-\alpha))^{1/3} \qquad (5)$$

Thus, according to equation (4), a value of $\sqrt{2k}$ can be obtained as the slope of the line which approximates this relationship as long as the linear relationship between x and $\sqrt{Ct}$ is observed.

2.2 Model to Predict Expansion

In order to predict the expansion ratio of mortar bars, at first, it is necessary to obtain total amount of reaction products in unit volume of mortar prisms. The total amount of reaction products (Tp : mol/l-mortar) can be calculated by following equation with the factors determining the proportion of mortar prisms.

$$Tp = A / 60.08 * \Sigma \alpha i \beta i \qquad (6)$$

where, A is total weight of aggregates in unit volume of mortar bars (g/l-mortar), 60.08 indicates molecular weight of SiO_2. βi and αi represent the volume fraction and volume reaction ratio of the aggregate with equivalent radius Ri, respectively.

If the linear relationship between the expansion ratio and the total amount of reaction products in mortar bars is assumed, the expansion ratio can be easily obtained by multiplying the total amount of reaction products by experimental constant. However, in recent years, some authors have shown that this relationship can not be expressed as a simple linear relationship. Nixon et al (1) investigated a pessimum expansion behavior of concrete bars with different content of reactive flint aggregate, and found that the expansion ratio of concrete bars with low flint content was larger than that of the concrete bar with high flint content, although the amount of reaction products (soluble silica) in concrete bar with low reactive flint content was less than that in concrete bar with high flint content. Diamond et al (2) also found that large alkali ions consumption occurred at the early stage of ASR without showing significant expansion. Therefore, following model to predict the expansion ratio of mortar bars is presented with some assumptions that can explain the different aspects of the progress of ASR and the expansion in mortar bars.

Many authors have shown that porous zone is existing in the cement matrix surrounding aggregates in concrete (Barnes et al (3),Grandet and Ollivier(4) and Ping et al(5)). Assuming that the reaction products of ASR are absorbed in this zone, the volume of such zone is proportional to the surface area of aggregate, and following equation is obtained to calculate total absorbed reaction products (silica) in unit volume of mortar prisms (Ta ; mol/l–mortar).

$$Ta = A * B * \Sigma \beta i / Ri \qquad (7)$$

where, B is a constant to convert the volume of the absorbing zone into molecular number of silica being absorbed. The model further assumes that only the reaction products which exceed the capacity of the absorbing zone can induce the expansion, and that the expansion ratio is simply proportional to the amount of reaction products exceeding the capacity of the absorbing zone, the following equation is obtained to predict the expansion ratio (ε ; %) of mortar bars.

$$\varepsilon = E * (Tp - Ta) \qquad (8)$$

where, E is a constant to convert the amount of reaction products causing expansion into the expansion ratio of mortar bars.

The unknown values in this model, B and E, can be obtained mathematically. According to equation (8), E can be obtained as the slope of the line which approximates the relationship between the calculated total amount of reaction products (Tp) and the observed expansion ratio of mortar bars (ε), as long as a good linear correlation is observed in this relationship. Furthermore, since the intercept of this approximated line indicates the value of (–E*Ta), Ta and B, also can be calculated by equation (7).

2.3 Calculation Process

In the calculation procedure, at first, the thickness of the reacted layer (x) and total amount of reaction products (Tp) are calculated. As stated above, the model to approximate the extent of ASR is a non linear model consisting of equations (1) and (2). Therefore, the value of x should be calculated by "step–by–step" integration of equation (1) with sufficiently short calculation time steps. In this calculation step, the latest value of alkali ion concentration in pore water (C) is used, thus the value of C also has to be calculated in this step.

Secondly, by comparing the calculated total amount of reaction products (Tp) with the observed expansion ratio (ε), the expansion ratios can be calculated by using the constants B and E.

Whole calculation process in predicting the expansion behaviors of mortar bars is summarized and shown in Figure 2.

From now on, the authors name the represented calculation method as " Uomoto–Furusawa–Ohga method " and abbreviate this to " U.F.O. method ".

3. EXPERIMENTAL EVALUATION OF ALKALI DIFFUSION COEFFICIENT AND ALKALI–SILICA RATIO OF REACTION PRODUCTS

3.1 Tested Aggregates

The reactive aggregates can be mainly divided into two groups by the difference of the expansion behaviors observed in the mortar bar method. One aggregate group shows the expansion behavior in which the expansion rate reduces with time (aggregate group showing decreasing rate expansion), and the other shows the expansion behavior in which the expansion rate is constant or increases with time (aggregate group showing constant rate expansion). The model proposed here should have sufficient accuracy in predicting the both typical expansion behaviors. Hence, the aggregates from both groups whose expansion behaviors were already reported by Tamura et al (6), are tested in this work. Quartz glass particle as the model of homogeneous aggregate is also tested. The properties of tested aggregates are shown in Table 1.

3.2 Test Conditions

The leaching test is performed basically in accordance with the quick chemical method defined as ASTM C 289. However, the amount of soluble silica and consumed alkali are measured with the passage of time. Furthermore, in order to evaluate the effect of temperature on alkali diffusion coefficient, the test is performed at various temperatures.

3.3 Results and Discussions

All the results obtained by the leaching test are shown as the relationship between the values of x and $\sqrt{Ct}$. Figure 3 indicates the results of quartz glass particle and the aggregate showing decreasing rate expansion at 80 °C. In this figure, the relationships can be approximated as a line except that the value of x measured at the latest period of the results of quartz glass particles is less than the approximated value. This is due to the value can not exceed the solubility of silica. Therefore, the alkali diffusion coefficients in the aggregates showing decreasing rate expansion are easily calculated from the slopes of these lines.

Figure 4 shows the results of the aggregates showing constant rate expansion at 80°C. As can be seen from this figure, it is found that the value of x increases slightly with increase of $\sqrt{Ct}$ at early stage of ASR, after that, x increases significantly with increase of $\sqrt{Ct}$. This relationship can be approximated as a bilinear relationship. Furthermore, it is also found that the values of x at the points where the slope of line changes are almost same through all the aggregates in this group. These results show that the alkali diffusion coefficients of the aggregates showing constant rate expansion behaviors increase during reaction. If the diffusion coefficient before it increases is named as initial diffusion coefficient (kin), and the increased diffusion coefficient is named as post diffusion coefficient (kpost), the progress of ASR of the aggregates showing constant expansion should be expressed by following equations.

Before diffusion coefficient changes,

$$dt / dx = kin\, C / x \qquad (9)$$

After diffusion coefficient changes,

$$dt / dx = kpost\, C / x \qquad (10)$$

Figure 5 shows the relationship between the amount of dissolved silica (Sc ; mol/l) and consumed alkali (Rc ; mol/l) obtained by the test on the aggregate No1. The result indicates that the relationship between Sc and Rc can be approximated as a straight line with a intercept on vertical axis (Rc). This fact is observed in the results of all the aggregates tested here. This result suggests that ASR begins with a large alkali consumption by the reactive aggregate without producing significant amount of reaction products. After that, alkali is consumed proportionally to the amount of dissolved silica. Therefore, the slope of the approximated lines shown in Figure 5 is estimated as indicating the value of RS (alkali-silica ratio of reaction products) after the large alkali consumption is finished, and the alkali consumption efficiency should be determined by both the amount of initially consumed alkali and RS. Since it is found that the amount of initially consumed alkali is not simply proportional to the amount of dissolved silica, equation (2) should be rewritten as,

$$C = (Cin - C(in.cons.) - Tp^{*}RS) / W \qquad (11)$$

where, Cin. and C(in.cons.) indicate the amount of alkalis in pore water before ASR starts and initially consumed alkali in unit volume of mortar prisms, respectively (mol/l-mortar). W is the amount of pore water in unit volume of mortar prisms(kg/l-mortar). Thus, the alkali consumption efficiency is higher with higher amount of initially consumed alkali and higher RS. The obtained values (amount of initially consumed alkali and RS) are shown in Table 2. It is considered that this large alkali consumption occurs in order to saturate the surface of the reactive aggregates with alkalis for ensuing destruction of aggregate texture. However, further studies such as petrochemical study are necessary to obtain better understandings on this phenomenon.

The results of aggregate No.1 (decreasing rate expansion type) and aggregate No.4 (constant rate expansion type) at various temperatures are shown in Figures 6 and 7, respectively. It is found that the slopes of the lines which approximate the relationships between x and $\sqrt{Ct}$ are increasing with increase of temperature. Generally, effect of temperature on diffusion coefficient can be expressed by Arrhenius's equation. Thus, the effect of temperature on the alkali diffusion coefficient obtained here are evaluated by using following modified Arrhenius's equation.

$$\log k = En\,(1/T) + Vinf \qquad (12)$$

where, En and T represent activation energy and absolute temperature, respectively. And Vinf can be defined as a limiting value of logarithm of diffusion coefficient. The results are plotted according to the equation (12) and shown in Figure 8. As shown in Figure 8, good linear relations corresponding to the Arrhenius's equation can be found . The leaching test performed here is an accelerating test by rather high temperatures. In order to calculate the expansion behaviors of mortar bars, the alkali diffusion coefficients at temperature of mortar bar test condition (40 °C) should be obtained. Since, good agreement of the test results with the Arrhenius's equation is found by this work, the alkali diffusion coefficients at 40 °C can be calculated by equation (12).

4. COMPARISON BETWEEN CALCULATED AND OBSERVED EXPANSION BEHAVIORS

Figure 9 shows the relationship between the calculated total amount of reaction products (Tp) and the observed expansion ratios of aggregates No.3 to No.6. As shown in this figure, a good linear correlation is observed. Then, it is confirmed that the constants B and E can be obtained by the simple way presented above.

Figures 10 and 11 show the calculated and observed expansion curves of the aggregate No.1, respectively. From these figures, it is found that the calculated expansion curves are similar to the observed expansion behaviors, and also shows the decreasing rate expansion behavior. Figures 12 and 13 show the calculated and observed expansion curves of the aggregates showing constant rate expansion behaviors, respectively. A good similarity between calculated and observed expansion curves also can be observed. In particular, the times where the calculated expansion ratio suddenly increase are almost coincide with that in observed expansion curve.

From the results obtained in this work, it is recognized that evaluating the reactivity of the aggregates showing both decreasing and constant rate expansion behaviors by using the model proposed here, is very useful in order to judge the reactivity of aggregate quantitatively in short time.

The calculation step 1 finishes when the alkali concentration in pore water becomes less than 0.1 mol/l as shown in Figure 2. The calculations for aggregates showing constant rate expansion behaviors are not finished at the age of 6 months. Therefore, the ultimate expansion ratios of the aggregates No.3 to No.6 are calculated and shown in Table 3. As shown in Table 3, the calculated ultimate expansion ratio of aggregate No.6 is almost same as that of aggregate No.3 which shows the largest expansion ratio at 6 months. The result indicates that the aggregate No.6 has almost same potential deterioration as aggregate No.3, although the expansion ratio of aggregate No.6 at 6 months is lower than that of the aggregate No.3. This is due to the alkali consumption efficiency of aggregate No.6 determined by the combination of the amount of initially consumed alkali and RS is almost same as that of aggregate No.3.

5. CONCLUSIONS

Since the good similarity between the observed expansion behaviors and the expansion curves calculated by the model proposed here is observed, the usefulness of the model is confirmed in evaluating the reactivity of the aggregate quantitatively in short time. And the difference of ASR mechanism in the aggregates showing variable expansion behaviors is also found by this work.

Furthermore, since effect of temperature is explained by this model, the potential reactivity of aggregates under the condition where the actual concrete structures are placed can be evaluated by extending this model.

However, the proposed model is based on many assumptions, and these should be verified experimentally. In particular, the relationship between the expansion ratio and the amount of total reaction products has not been studied in this work experimentally. The authors are now planning to perform some experiments in order to obtain better understandings on this relationship, and also to improve the model proposed here.

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TABLES AND FIGURES

Table.1 Properties of Aggregates

No.	*Type of rocks*	*Exp. behavior*
1	*Andesite*	*convergent exp.*
2	*Quartz glass*	*(conv. exp.)*
3	*Sandstone*	*continuous expansion*
4	*Sandstone*	
5	*Sandstone*	
6	*Sandstone*	

Table.2 Factors Concerning to Alkali-Consumption Efficiency

No.	*RS (mol/mol)*	*initially consumed alkali (mol)*
1	*0.138*	*0.058*
2	*0.064*	*0.033*
3	*0.243*	*0.070*
4	*1.122*	*0.031*
5	*0.509*	*0.051*
6	*0.344*	*0.018*

Table.3 Calculated Ultimate Expansion Ratio (%)

No.3	*0.587*
No.4	*0.165*
No.5	*0.319*
No.6	*0.576*

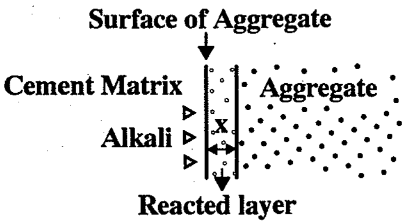

Fig.1 Reaction at Surface of Aggr.

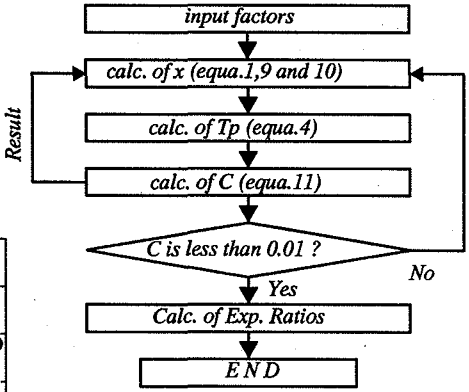

Figure.2 Calculation Process

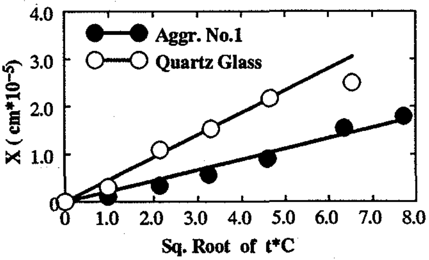

Figure.3 Results of Leaching Test
(convergent expansion type)

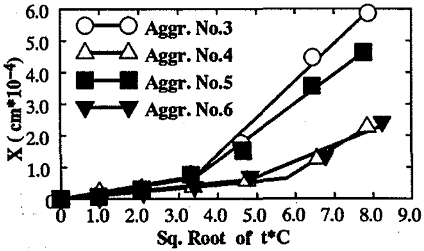

Figure.4 Results of Leaching Test
(continuous expansion type)

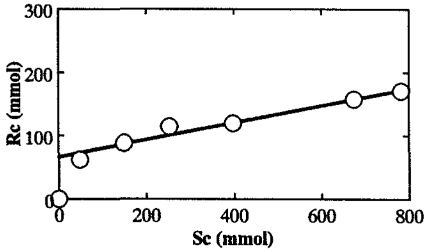

Figure.5 Relationship between Sc and Rc

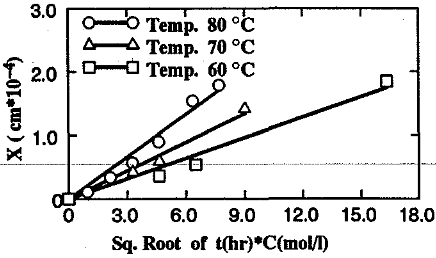

Figure.6 Results of Leaching Test (Aggr. No.1)

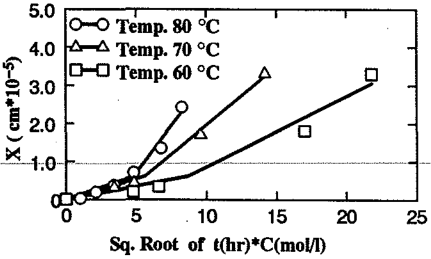

Figure.7 Results of Leaching Test (Aggr. No.4)

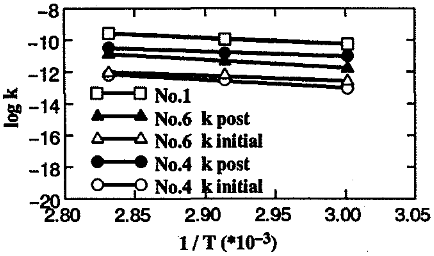

Figure.8 Efeect of Temperature

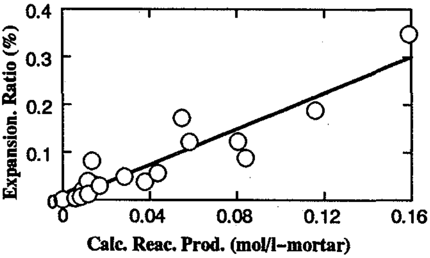

Figure.9 Comparison between Calc. Reac. Prod. and observed Exp. Ratios

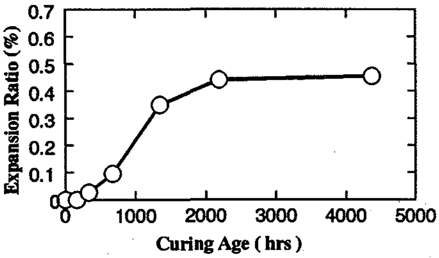

Figure.10 Observed Expansion Behavior (decreasing rate exp. type)

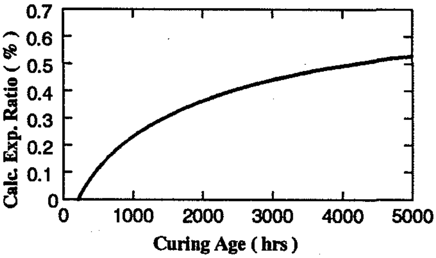

Figure.11 Calc. Expansion Behavior (decreasing rate exp. type)

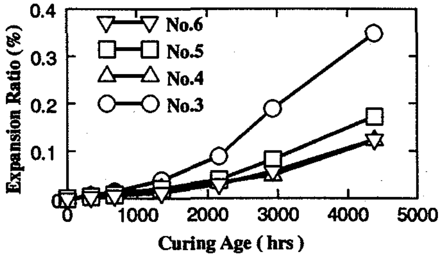

Figure.12 Observed Expansion Behaviors (constant rate exp. type)

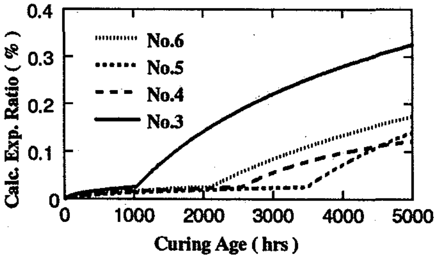

Figure.13 Calculated Expansion Behaviors (constant rate exp. type)