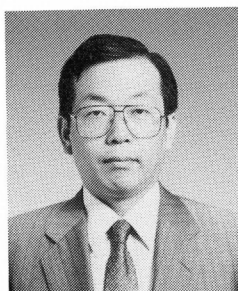
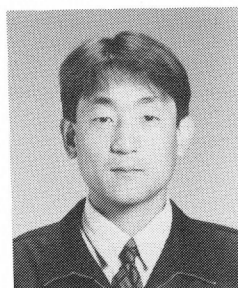


A Simple Model for Predicting Expansion in Mortar Bars due to Alkali-Silica Reaction

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SYNOPSIS

An attempt has been made to present a kinetics-based model to predict the progress of alkali-silica reaction (ASR). The model incorporates the effect of such variable factors as size and reactivity of aggregate, alkalinity of cement matrix.

This model can simulate the observed expansion behaviors in mortar bars with different alkali content, and pessimum effects of reactive aggregate content on expansion. On the basis of the proposed model, the mechanism of inorganic admixture in reducing the expansion in mortar bars due to ASR is also discussed in this paper.

keywords: alkali aggregate reaction, model, kinetics, diffusion theory

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1. Introduction

The alkali-silica reaction (ASR) has been identified as one of the main causes for premature deterioration of concrete structures, and many papers have been published dealing with various aspects of this mechanism and its effects. In order to prevent deterioration of ASR, it is important to evaluate the reactivity of aggregate before it is used, and the mortar bar test defined as ASTM C 289 and JIS A 5308 is widely used for the sake of this evaluation. In the mortar bar test, the reactivity of aggregate is classified by the expansion ratio of mortar bars at the curing age of 6 months which can exceed 0.1% (deleterious) or not (inert). However, it is reported that the ultimate expansion ratio of mortar bars made with certain types of aggregate exceeds 0.1% even though the expansion ratio at 6 months is less than 0.1%. Such aggregates classified as inert by the mortar bar test are considered to have high potential reactivity. Therefore, a comprehensive model to predict the progress of ASR and the expansion behavior of mortar bars (including the ultimate expansion ratio) is required to evaluate the reactivity of such types of aggregates. Furthermore, the model should evaluate the reactivity of all the aggregates in a more quantitative manner and also be useful to predict the progress of ASR in actual concrete structures which have already been built using reactive aggregates.

Some researchers have tried to establish a model to predict the expansion behavior of mortar bars. For example, the model proposed by Hobbs¹⁾ can simulate the pessimum effect of Beltane opal content on expansion, and Chatterji and Chrivtensen tried to predict the expansion of mortar bars cured in sodium chloride solution²⁾. However, these models are appreciable only under limited conditions (type of aggregate, curing condition etc.). In order to establish a model which is applicable to a broad range of aggregates under variable conditions, the reaction itself should be simplified by using a proper theory.

ASR is one of the typical chemical reactions occurring in a solid-liquid system. Diffusion theory gives good results in approximating the progress of many reactions occurring in a solid-liquid system. Thus, the authors utilized diffusion theory to express the progress of ASR. The proposed model can predict expansion behavior by using the calculated amount of reaction products in mortar bars. Comparisons between experimentally observed and predicted expansion behavior are also shown in this paper.

2. Fundamental Principles of Model

ASR is considered to occur in stages. Under the assumption that the rate-determining stage of ASR is diffusion of alkali ions from the surface into the reactive aggregates, and that the alkali diffusion stage can be explained by conventional diffusion theory, the following equation is derived from Fick's first law to approximate the thickness of the reacted layer as shown in Figure 1:

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

Here 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. Equation (2) which describes the thickness of the reacted layer is obtained by integrating equation (1).

$$x = \sqrt{2kCt} \quad (2)$$

If we further assume a spherical aggregate, the volume reaction ratio (α) of individual aggregate particles with radius R (cm) can be written as

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

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

$$C = f(RS, \sum \alpha_i \beta_i) \quad (4)$$

Here, β_i represents the volume fraction of the aggregate with radius R_i to total amount of aggregate.

As can be seen from the interrelationship between equations (1) and (4), the model is defined as a typical non-linear model.

3. Alkali Consumption and Movement in Cement Matrix

Since the ASR occurs at the surface of reactive aggregate, it is considered that the alkali ions are also consumed at the surface of reactive aggregates. Thus, in cement matrix, a difference in alkali concentration between the surface of aggregate and points which are sufficiently far from the surface may be observed. In that case, the value of C in equation (1) should be calculated accurately as the concentration at the surface of aggregate, considering the distribution of the alkali ion concentration formed in cement matrix. However, as reported by Goto³⁾, the diffusion coefficients of alkali ions in cement matrix are sufficiently large (about 10^{-8} cm²/sec), and this high mobility of alkali ions may decrease and ease the concentration difference. The authors precalculated the distribution of alkali ions in cement matrix assuming an extremely by high rate of ASR such that the alkali ions are used up in 30 days at the surface of reactive aggregate. As a result, the alkali concentration difference between the surface of aggregates and the bulk point in cement matrix is kept to less than 3% during the simulated reaction. Thus, the authors decided to ignore the concentration difference in cement matrix and assumed that the alkali ion concentration in cement matrix is always kept constant during the reaction. As a result, the function expressed in equation (4) can be rewritten as the following:

$$C = C_{in} - k_{con} \sum \alpha_i \beta_i, \quad (5)$$

Here C_{in} and k_{con} represent the initial alkali content in the cement matrix and the experimental constant required to calculate the consumed alkali from the amount of reacted silica. C_{in} can be obtained by the equation presented by Diamond⁴⁾ et al. as a function of the alkali content in cement, and the constant k_{con} includes the effect of the alkali-silica ratio of reaction products.

4. Model to Predict Expansion

In order to predict the expansion ratio in mortar bars, at first it is necessary to obtain the total amount of reaction products in unit volume of mortar prisms. If the linear relationship between the expansion 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 an experimental constant. However, in recent years, some authors have shown that this relationship cannot be expressed as a simple linear relationship. Nixon et al.⁵⁾ investigated the pessimum expansion behavior of concrete bars with different content levels of reactive flint aggregate, and found that the expansion ratio of concrete bars with low flint content was larger than that of the concrete bars with high flint content, although the amount of reaction products (soluble silica) in concrete bars with low reactive flint content was less than that in concrete bars with high flint content. They attempted to explain this phenomenon in terms of the total surface area of reactive aggregate, in which case, the total surface area of reactive aggregate increases linearly with the reactive aggregate content. They presented the following suggestions for the effect of total surface area increase in preventing expansion. i) Chemical composition of reaction products changes such that water is not absorbed. ii) Volume of pores in cement paste around the reactive aggregate increases such that pores can absorb reaction products.

Furthermore, other researchers have shown that a porous zone exists in the cement matrix surrounding aggregate in concrete (Barnes et al.⁶⁾, Grandet and Ollivier⁷⁾ and Ping et al.⁸⁾). Therefore, the authors assumed that the reaction products of ASR are absorbed in this zone and that the volume of such a zone is proportional to the surface area of reactive aggregate. On the basis of the above discussions, the following equation is obtained to calculate the total amount of absorbed reaction products (silica) in unit volume of mortar prisms (Ta : mol/l-mortar).

$$Ta = A \cdot B \cdot \sum \beta_i / R_i \quad (6)$$

Here, B is an experimental constant required to calculate the number of silica molecules being absorbed from the volume of such a zone. Hereafter, this zone is referred to as "the absorbing zone" in this paper. 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 : %):

$$\epsilon = E \cdot (T_p - T_a), \quad (7)$$

Here, E indicates the constant required to calculate the expansion ratio of mortar bars from the amount of reaction products causing expansion, and T_p represents the total amount of reaction products in equation (8).

$$T_p = A / 60.08 \cdot \sum \alpha_i \beta_i \quad (8)$$

Here, A is the total weight of aggregates in unit volume of mortar bars (g/l -mortar), and 60.08 is the molecular weight of SiO_2 .

The unknown values in this model, B and E , are defined mathematically. According to equation (7), E can be obtained as the slope of the line which approximates the relationship between the calculated total amount of reaction products (T_p) 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 $(-E \cdot T_a)$, T_a and B , can also be calculated by equation (6).

5. Calculation Process

In the calculation procedure, first, the thickness of the reacted layer (x) and total amount of reaction products (T_p) should be obtained. As stated above, the model to approximate the progress of ASR is a nonlinear model consisting of equations (1) and (5). Therefore, the value of x is calculated by "step-by-step" integration of equation (1) with sufficiently short calculation time steps. In this calculation step, the most recently obtained value of alkali ion concentration in pore water (C) is used, thus the C value also has to be calculated in this step. The unknown values in this calculation step, the diffusion coefficient of alkali in reactive aggregates (k) and the experimental constant required to calculate the consumed alkali from the amount of reacted silica (k_{con}), are also obtained mathematically.

Secondly, by comparing the calculated total amount of reaction products (T_p) with the observed expansion ratio, the unknown values in the model required to calculate the expansion ratio, B and E , are defined by the procedure mentioned above.

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

6. Comparison between Calculated and Observed Expansion Behavior

6.1 Expansion of Mortar Bars with Different Alkali Content

Figure 3 shows the experimentally observed⁹⁾ and calculated expansion behavior of mortar bars with different alkali content. As shown in this figure, the calculated results can simulate the actual expansion curves accurately. In particular, a high degree of similarity is observed in the phenomena in which the ratios between ultimate observed expansion are larger than the ratios between alkali content.

In order to obtain a better understanding of the simulation, the calculated total capacity of the absorbing zone and the amount of reaction products in each mortar bar are shown in Figure 4. Under this condition, the factors concerning mix proportion of mortar bars, such as total reactive aggregates (A : g/l -mortar) and particle size distribution of reactive aggregate ($\sum \beta_i$) are kept constant across all the mortar bars. Thus, as can be seen from equation (6), the total capacity of the absorbing zone is also kept constant. The calculations used to obtain the total amount of reaction products were performed until the alkali concentration became less than 0.1% for all cases. Therefore, the ultimate total amount of reaction products is proportional to the initial alkali content. As mentioned previously, in this model, it is assumed that the difference between the total amount of reaction products and the total capacity of the absorbing zone is proportional to the expansion ratio, which is why the ultimate expansion ratios are not proportional to the alkali content in this model.

The mechanism of critical alkali content (a phenomenon in which significant expansion in a mortar bar is ob-

served only as the alkali content exceeds a certain level) can also be explained by the model as follows. In this model, if the total amount of reaction products cannot exceed the total capacity of the absorbing zone, no expansion is observed. Thus, the critical alkali content can be understood as the amount of alkali sufficient to produce the amount of the reaction products which exceeds the total capacity of the absorbing zone.

6.2 Pessimism Effect of Reactive Aggregate Content on Expansion

Figure 5 indicates expansion behaviors of mortar bars with different reactive aggregate content reported by Mori and Kobayashi⁹⁾. As shown in this figure, a typical pessimism effect of reactive aggregate showing maximum expansion ratios at the content level of 60% can be observed. The calculated result is shown in Figure 6. From these figures, it is found that the calculated expansion behavior is very similar to the observed behavior. In particular, the phenomenon in which the peak at 60% becomes sharper with the passage of time is well simulated.

The proposed model can also explain the pessimism effect of reactive aggregate content on expansion. In this case, the total capacity of the absorbing zone is proportional to the reactive aggregate content. However, as indicated in equation (5), alkali ion concentration decreases with the increase of the amount of the total reaction products. Thus, as can be seen from the interrelationship between equations (2), (3) and (5), the average reaction ratio of reactive aggregate decreases with the increase in reactive aggregate content. The total amount of reaction products is obtained by multiplying the summation of $\alpha_i \beta_i$ by the total weight of reactive aggregate. Thus, the amount of total reaction products increases with increase in reactive aggregate content even though the average reaction ratio decreases with increase in reactive aggregate content. However, this increasing tendency is not linear with the reactive aggregate content due to the effect of low average reaction ratio. The increasing tendency of the total capacity of the absorbing zone and the total amount of reaction products to the reactive aggregate content is shown in Figure 7, and the maximum difference between two lines appears at the reactive aggregate content of 60%. In this model, since this difference is defined as proportional to the expansion ratio, the pessimism effect of reactive aggregate content can be simulated.

7. Discussion on Mechanism of Inorganic Admixture in Reducing Expansion

Many papers have been published dealing with the effect of inorganic admixtures, such as slag, fly ash and silica fume, in reducing the expansion due to ASR. Fujisaki et al. have carried out an experiment¹⁰⁾ on the effect of finely ground glass powder (average radius is around 10 μ m) in reducing expansion. The properties of the glass powder are very similar to those of inorganic admixtures as both glass powder and inorganic admixtures have extremely large surface area and high reactivity. Thus, it is useful to analyze the results of this experiment in order to obtain a better understanding of the mechanism of the expansion-reducing effect of inorganic admixtures.

In this experiment, three types of glass powders shown in Table 1 were added to replace the cement content of the mortar bars made with Pyrex glass as fine aggregate. In Table 1, the results of a quick chemical test defined as ASTM C 289 for each glass are also indicated. The observed expansion curves are shown in Figures 8 (replacement ratio of glass powder to cement is 5%) and 9 (replacement ratio of glass powder to cement is 10%). As can be seen from these figures, the use of quartz glass powder and Pyrex glass powder can reduce the expansion corresponding to the replacement ratio. On the other hand, the use of plate glass powder accelerates the expansion.

Under the assumption that the progress of ASR in the quick chemical test is explained by the model proposed here, the diffusion coefficient of alkali in reactive aggregate can be calculated from the results of the quick chemical test by following the procedure outlined below.

Initially, C and α values are defined as 1 mol/l and 0 when the time t is zero, respectively. Since C and x values when time t is 24 (hrs) can be calculated from the results of a quick chemical test by using equations (3) and (5), the diffusion coefficients of alkali in each type of glass can be obtained by analyzing this data mathematically with equation (1). The alkali-silica ratio of reaction products, which is considered to be an important factor for defining the alkali consumption efficiency during reaction, is obtained directly from the result of the quick chemical test as R_c/S_c . The diffusion coefficients at a temperature of 80 °C can be calculated by the

procedure mentioned above. However, it is necessary to obtain the diffusion coefficient at 40 °C to predict the progress of ASR in mortar bars. In this experiment, the value of the activation energy of the diffusion coefficient of alkalis in quartz powder reported by Suzuki et al.¹¹⁾ is applied to convert the diffusion coefficients from 80 °C to 40°C.

Figures 10 and 11 show the predicted expansion behavior. As can be seen from these figures, good agreement is observed between the experimentally obtained and calculated expansion behavior. In particular, the calculation can simulate the difference in ability in reducing the expansion corresponding to the type and replacement ratio of glass powder.

In these cases, all the calculations are completed when the alkali is used up. The reaction products from glass powder do not contribute to the expansion, because of their extremely large surface area (total capacity of the absorbing zone). Thus, from the viewpoint of total capacity of the absorbing zone, the expansion ratios with different types of glass powder should not differ so much. The difference in effectiveness of glass powder in reducing the expansion can be related to the difference in the alkali-silica ratio of reaction products (Rc/Sc) of each glass powder. As mentioned previously, the values Rc/Sc, obtained from the results of the quick chemical test, are used to calculate the alkali concentration in mortar bars. These values are defined as indicating the alkali consumption efficiency. For example, for the same amount of reaction products (dissolved silica), the reaction with higher Rc/Sc can consume a greater amount of alkali. The alkali which cannot be consumed by glass powder contributes to the reaction with Pyrex glass aggregate. Since the radius of Pyrex glass aggregate is relatively large and the total capacity of the absorbing zone is small compared to that of well-ground glass powder, the reaction products of the Pyrex glass aggregate can induce the expansion. In other words, a higher Rc/Sc value of reaction products of glass powder can reduce the alkali which induces expansion. As can be seen from Table 1, the Rc/Sc value of quartz glass powder is the largest, and it can reduce the expansion most effectively. The Pyrex glass powder can also reduce expansion, but the effectiveness is lower than that of quartz glass powder, because of the relatively lower value of Rc/Sc. On the other hand, the Rc/Sc value of plate glass powder is negative. Thus, plate glass powder itself can release alkali during reaction and increase the alkali which can induce the expansion.

From the above discussion, the mechanism of the effectiveness of inorganic admixtures in reducing the expansion can be concluded to be the difference in alkali consumption efficiency. And excellent expansion reducer should have an extremely large surface area (total capacity of the absorbing zone) and high alkali consumption efficiency.

8. Conclusions

Since the similarity between the observed and calculated expansion behavior can be observed, the usefulness of the proposed model in predicting the expansion behavior of mortar bars due to alkali-silica reaction is confirmed. The mechanism of inorganic admixtures in reducing the expansion can also be formulated on the basis of the model.

However, the proposed model is still based on many assumptions. In particular, it includes many unknown factors such as activation energy. In this work, these factors are mainly obtained in a mathematical manner, while some of these factors should be defined experimentally corresponding to the type of reactive aggregate. Thus, further study to define these values is required. The authors are now investigating a simple test method which can define these values in a short time.

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Table 1 Tested Glass Powder

Type	Sc (mmol/l)	Rc (mmol/l)	Rc/Sc
Quartz Glass	1020	73	0.072
Pyrex Glass	720	15	0.021
Plate Glass	477	-168	-0.352

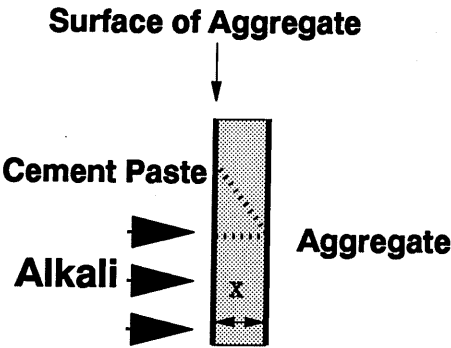


Fig.1 Reaction at Surface of Aggr.

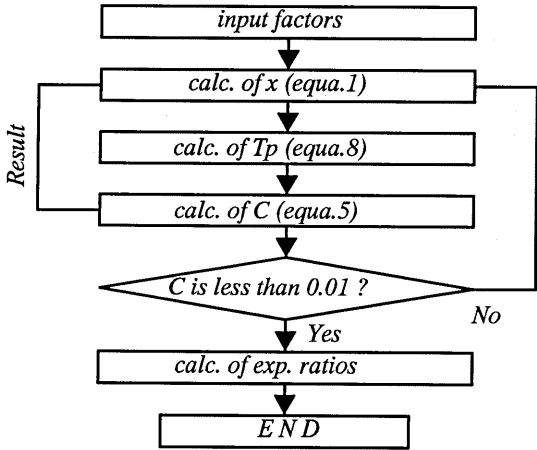


Fig.2 Calculation Process

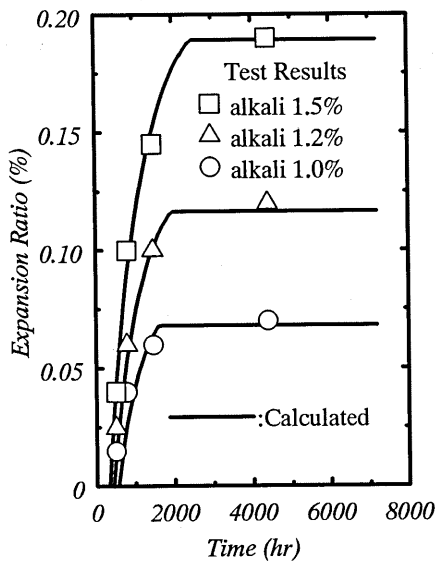


Fig.3 Expansion of Mortar Bars with Different Alkali Content

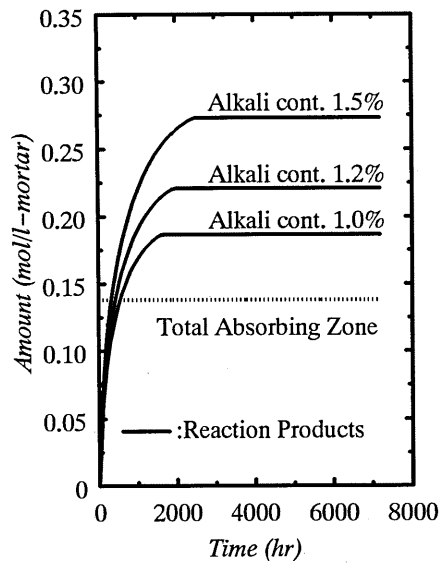


Fig.4 Relationship between Calc. React. Products and Total Absorbing Zone

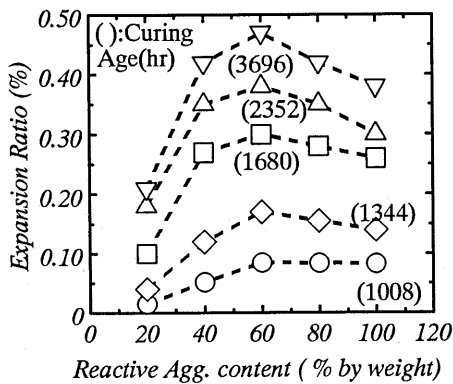


Fig.5 Observed Expansion Ratio

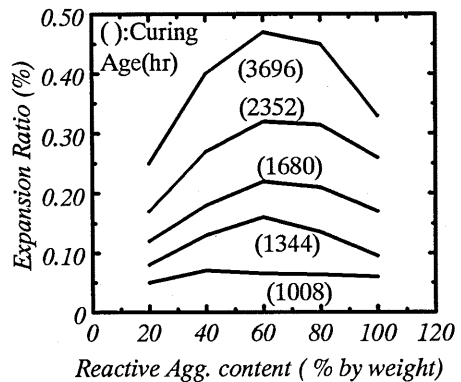


Fig.6 Calc. Expansion Ratio

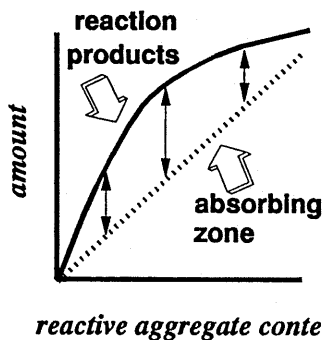


Fig.7 Relationship betw. Reaction Prod. and Total Abs. Zone

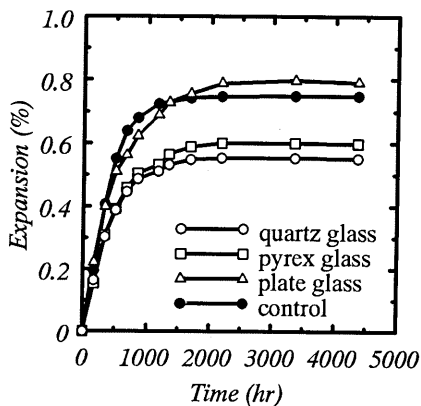


Fig.8 Effect of Glass Powder (rep. ratio 5%)

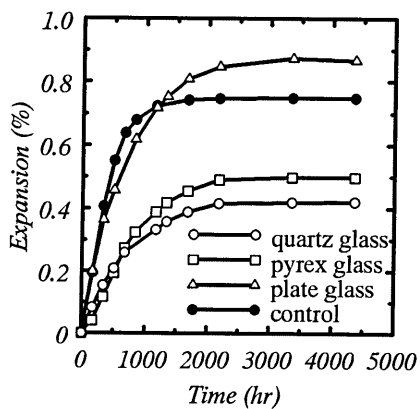


Fig.9 Effect of Glass Powder (rep. ratio 10%)

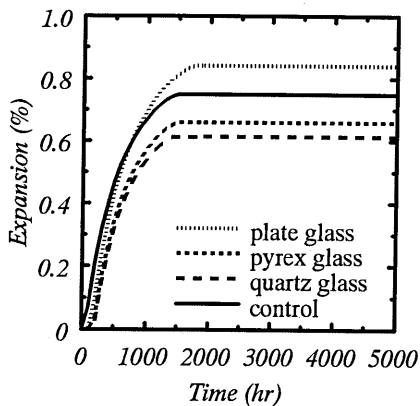


Fig.10 Calcu. Effect of Glass Powder (Rep. Ratio 5%)

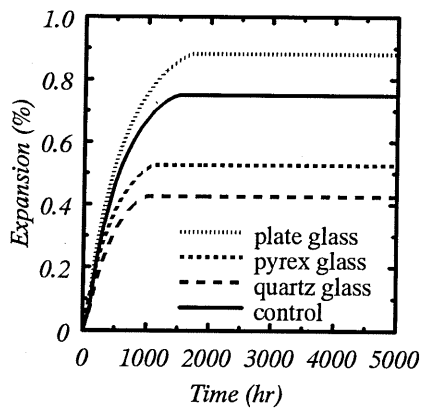


Fig.11 Calcu. Effect of Glass Powder (Rep. Ratio 10%)