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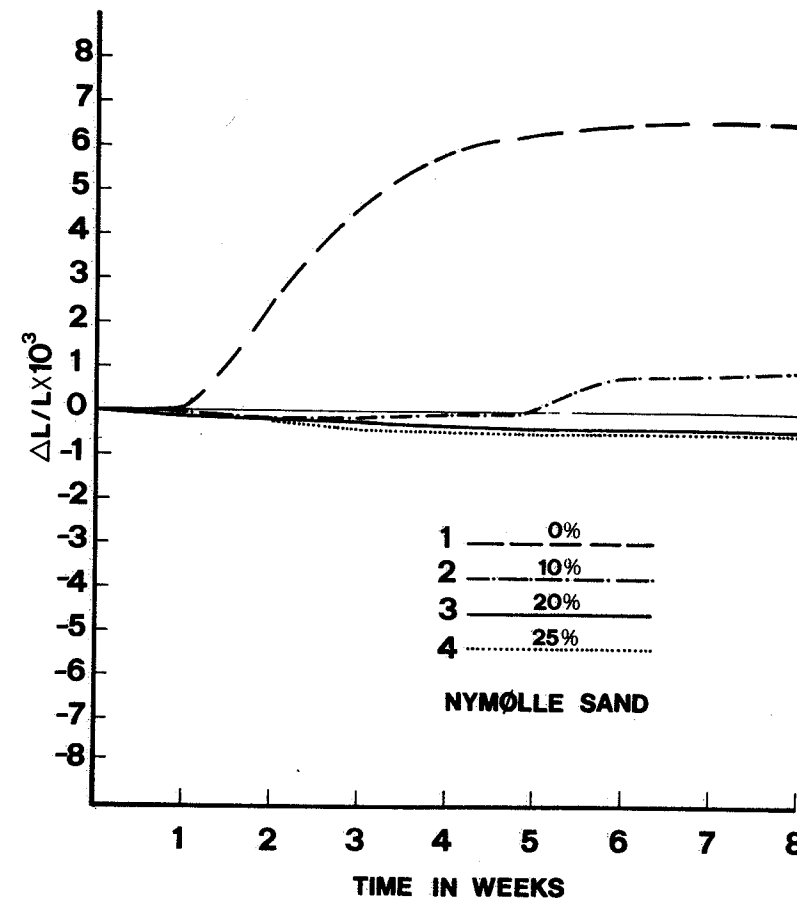


Fig. 3 Time-expansion curves of mortar bars made with Nymølle sand. Figs. in the diagram indicate the % molar content in cements.

ABSTRACT

Measurements of the rates of reaction between various aggregates and high alkali cement have been carried out under different temperatures. The aggregates studied include quartz, silica brick, fused silica, perlite and opal. Assuming the value of expansion of mortar bars being proportional to the amount of products of reaction, we can use the results of measurement of length change to express the rate of reaction. 1x1x4cm mortar bars of cement:aggregate=10:1 with w/c=0.3 and aggregate of sizes=0.15-0.75mm were made and demolded after a one-day curing, after which they were immersed in a 10% KOH solution and were treated at several temperatures. The results show that the rates of reaction of various aggregates are very well predicted by Arrhenius equation $K = K_0 \exp(-\frac{E}{RT})$. The correlation coefficients are 0.9756-0.9972. But the concordance for any one of them exists only in a narrow range of temperatures which vary for different aggregates. Besides, the values of E and K_0 are also different for different aggregates. According to these results, we assume that these values can be used to compare the relative alkali reactivities of various aggregates. It might be much better than to use only one value of expansion under a fixed temperature in order to identify the the alkali reactivity of aggregates. In addition, E and K_0 might be more accurate to express the intrinsic characteristics of aggregates.

KEY WORDS: Rate law, Arrhenius equation

1. INTRODUCTION

Mortar bar method (ASTM C227-71)(1), chemical method (ASTM C289-71)(2), rock cylinder method (ASTM C586-69)(3) and petrographic method (ASTM C295-65)(4) are usually used for identification of alkali reactivity of aggregates. During the past years the number of cases of deterioration of concrete caused by alkali-aggregate reaction in many countries has increased and more and more types of alkali reactive aggregates appeared. The methods mentioned above do not seem to be able to satisfy all our needs, and some authors even doubted the reliability of these methods(5). Moreover, a conclusion which is reliable is often wanted in practical work as quickly as possible. Therefore, many authors paid much attention to the methods for the identification of alkali reactivity of aggregate. Grattan-bellow(6) reported in more detail the various testing methods. Chatterja(7) and Regourd(8) suggested new rapid methods respectively.

We have found a new method which needs only two days for identify the alkali reactivity of an aggregate by measuring the values of expansion of mortar bars autoclave-treated in a 10% KOH solution(9). Through more than thirty kinds of aggregates being examined, it has been proved that the method can be used to distinguish the reactive aggregate from non-reactive one.

Among all these testing methods, the measurements of length change of mortar bars can quantitatively indicate the degree of alkali reactivity of aggregates. However, in all mortar bar methods, the values of expansion of bars cured at only one temperature are utilized to identify the reactivity, so it is impossible to know or predict the behaviour of aggregates at other temperatures. At present, the modern concrete technique tends to increase the proportion of cement in concrete and to shorten the time of construction. These factors would elevate the temperature of construction products considerably due to heat of hydration of cement, especially in mass concrete constructed in hot weather. The temperature can occasionally reach 80-90°C. Unsuch conditions, the behaviour of aggregates might be different from that in 20°C or 38°C. Herein the alkali-silica reaction rate dependence both on time and on temperature were studied. The results prove that the dependence on time is a linear correlation in a certain period and the dependence on time is quite well in agreement with Arrhenius equation within a range of temperatures.

2. EXPERIMENTAL METHOD

The experimental work done was similar to that described in reference (9), but with a little modification. The chemical composition of the cement is: CaO 65.13%, SiO₂ 20.60%, Al₂O₃ 5.50%, Fe₂O₃ 5.74%, MgO 0.87%, K₂O 0.39% and Na₂O 0.17%. The content of alkali with extra addition of KOH in mixing water is calculated in terms of Na₂O to be 1.5%. The aggregates include sand of quartz, opal, perlite, fused silica and silica brick. 1x1x4cm mortar bars were made by cement:aggregate=10:1, sizes of aggregates=0.15-0.75mm and w/c=0.3. These mortar bars were demolded after a one-day curing in moist chamber, their lengths measured as starting values, and then they were put in a 10% KOH solution and treated under different temperatures. The amount of 10% KOH is 10ml for each bar. The length changes were measured after different intervals of time.

3. EXPERIMENTAL RESULTS AND DISCUSSION

The results studied for the rate of alkali-silica reaction dependent on time and temperature are stated successively as follows:

3.1 Dependence on time

When the values of expansion of mortar bars are assumed to be proportional to the amount of products of reaction, the values of length change in the course of time can be used to express their rate of reaction. The dependence of expansion on time is illustrated in Fig.I(a,b,c).

The results in Fig.I show that there is a linear dependence of values of expansion on time, that is

$$\text{Rate of reaction } V = \frac{d\alpha}{dt} = K$$

Where α represents % of expansion, t , time(hours or months) and K , the rate constant of reaction.

Alkali-silica reaction is a liquid-solid reaction. During its process, OH⁻, K⁺ and Na⁺ ions diffuse into the inner part of solid particles. Therefore the rate of reaction(V) should depend on: (1) coefficient of diffusion (D), (2) thickness of reaction layer on the surface of the particle(δ), (3) area of reaction(A) and differences of ion concentrations(ΔC), and can thus be expressed with the following formula:

$$V \propto \frac{D}{\delta} A \Delta C$$

As the reaction goes on, the differences of ion concentrations(ΔC) will be reduced and the thickness will be increased, so the rate of reaction(V)

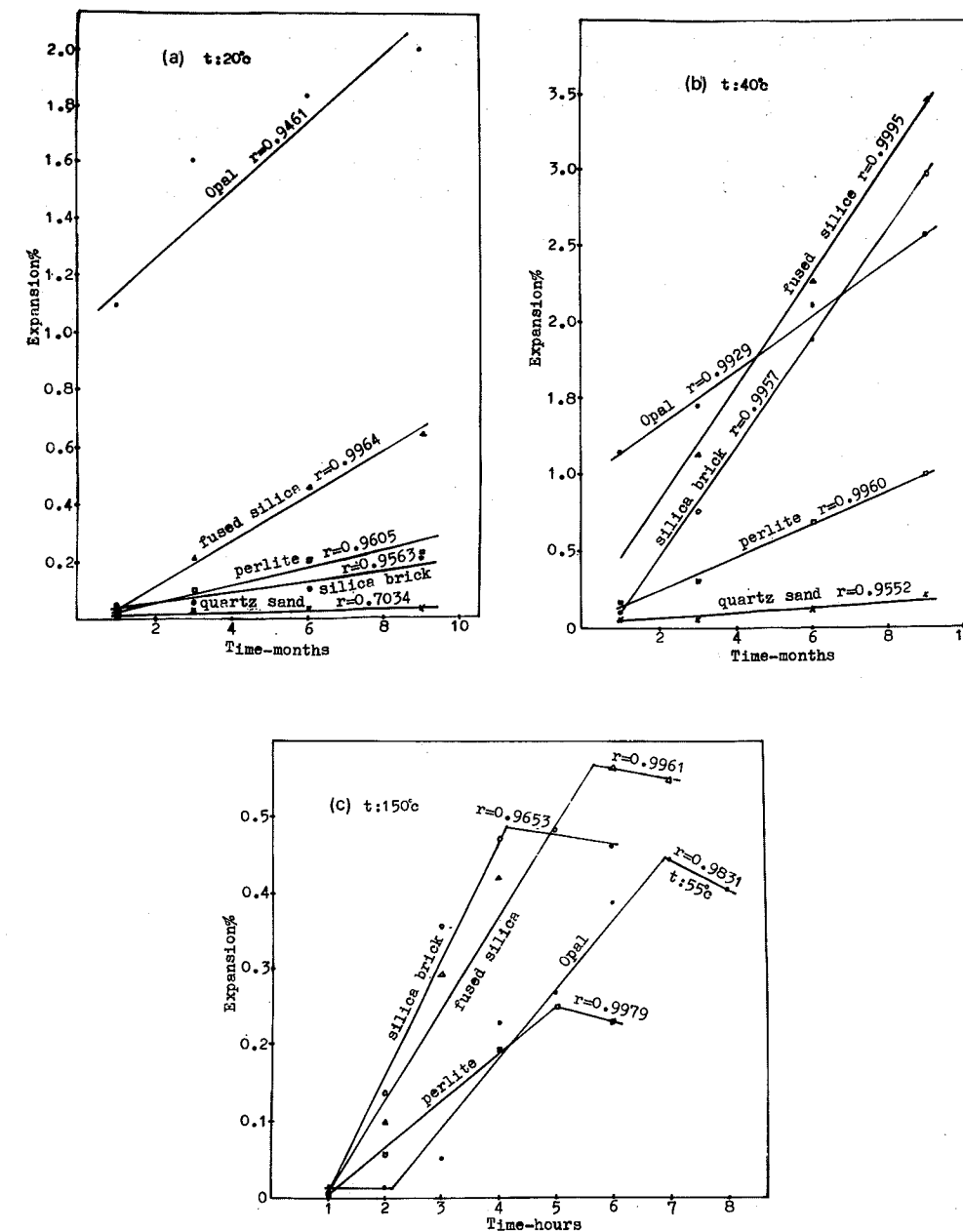


Fig.I Dependence of length change of mortar bars on time, (a) 20°C, cured in moist chamber, (b) 40°C, cured in moist chamber, (c) 150°C, autoclave-treated in a 10% KOH solution, only the mortar bars made from opal were cured in alkali solution at 55°C

must be correspondingly reduced in the course of time. But the experimental results showed that it is a linear dependence, which means the rate of reaction would not be reduced and remained a constant in the course of reaction. This may be due to the disintegration of the reactive particles, which is caused by the swelling by adsorption of water of the reaction products which are formed from the penetration of OH^- , K^+ , and Na^+ ions along the weakest position of the reactive particles. Through repeated observation, we noticed that one stage during the expansion process is characterised by the appearance of microcracks on the particles of reactive aggregate(10). In the course of reaction, the disintegration enlarges the area of reaction, and thus the newly formed surface might be exposed to reaction with alkali, which eliminates the effect of C and . It seems we could come to a conclusion that the alkali-silica reaction is pseudo-zero-order reaction.

Fig.1(c) shows that after a certain period the value of expansion does not continue to increase, on the contrary, it is slightly reduced. Observations under microscope proved that the particles of aggregates after this period were no longer present, and they had reacted almost completely. The products of reaction escaped but the holes remained. Under these conditions, no more stress of expansion was present, and the cracks already produced might even be sealed up again. The value of expansion was going to reduce slightly. So we may divide the whole expansion process of alkali-silica reaction into three periods as Fig.2 shows schematically: (1) a dormant period (AB), Though the alkali-silica reaction does take place in this period, no expansion will be observed, as the stress of expansion is not now big enough compared to the strength of mortar bar, (2) period of equal rate of expansion (BC), The value of expansion is proportional to the amount of reaction products, and there is a linear dependence of expansion on time, (3) period of decreasing rate of expansion(CD or CD').

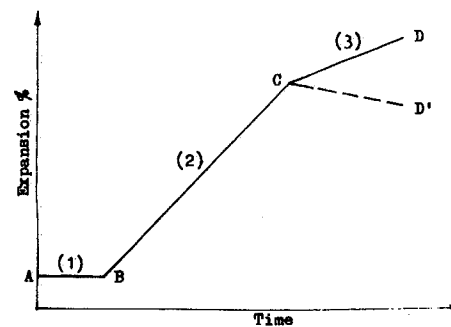


Fig.2 Schematic figure of the process of alkali-silica reaction

3.2 Dependence of reaction rate on temperature

With the help of the rapid method which is beneficial to investigate the behaviour of various aggregates under different temperatures, the values of expansion can be obtained in a short time. The moulding and curing of the mortar bars are similar to that described above, only with the difference that the bars are put in a 10% KOH solution and treated for 6 hours under different temperatures. The results are illustrated in Fig.3.

Fig.3 shows that the values of expansion of mortar bars made from all aggregates increase rapidly as the temperature is increased, which means that the temperature accelerates the rate of alkali-silica reaction considerably. Even the so-called inert aggregate(e.g. crystal quartz) reacts obviously when the temperature is over 150°C, and the mortar bars made from it would expand.

The results studied under SEM showed that like opal, the particles of quartz were seriously reacted at 180°C and 300°C, forming white gel and displaying cracks on bars. There were also many empty holes in bars at 300°C. So the distinction between inert and active aggregates is conditional, and serious alkali-silica reaction might take place in some inert aggregates under suitable condition.

Fig.3 also shows that the values of expansion of mortar bars autoclave-treated in a 10% KOH solution are not to increase at a certain limiting temperature, and there are different temperatures for different aggregates. For example, the limiting temperature is about 80°C for opal, and 120°C for silica brick and fused silica.

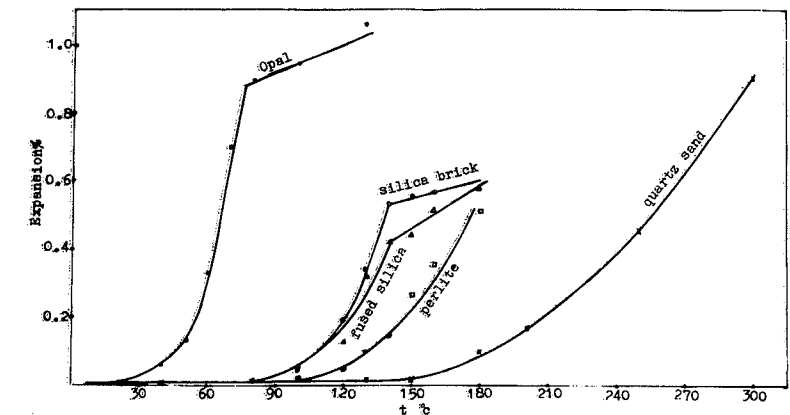


Fig.3 Values of expansion of bars treated in a 10% KOH solution for 6 hours at different temperatures

According to Glasstone(11): "The Arrhenius equation is widely applicable not only to homogeneous reaction, but also to reaction in solution and to heterogeneous processes. It frequently fails, however for chain reaction". The formula of Arrhenius equation is:

$$K = K_0 \exp\left(-\frac{E}{RT}\right)$$

Where: K-rate constant, K_0 -frequency factor, E-activation energy, R-gas constant, T-absolute temperature.

Alkali-silica reaction is a solid-liquid reaction. If we assume that the value of expansion is proportional to the amount of reaction products, then the value of expansion in a certain period(as 6 hours) can be used to express the rate of reaction at a fixed temperature. This means that the rate constant $K(\text{sec}^{-1})$ equals to the ratio of expansion% to 3600x6. Consequently, we can apply Arrhenius equation to alkali-silica reaction. The relationship between logarithm of rates($\lg K$) of alkali-silica reaction and $1/T$ is shown in Fig.4. The values of activation energy(E) and frequency factor(K_0) for various aggregates which were calculated by Arrhenius equation are shown in Table I.

The correlation coefficient shown in Table I are varied in the range of 0.9756-0.9972, Which proves that there is a close correlation.

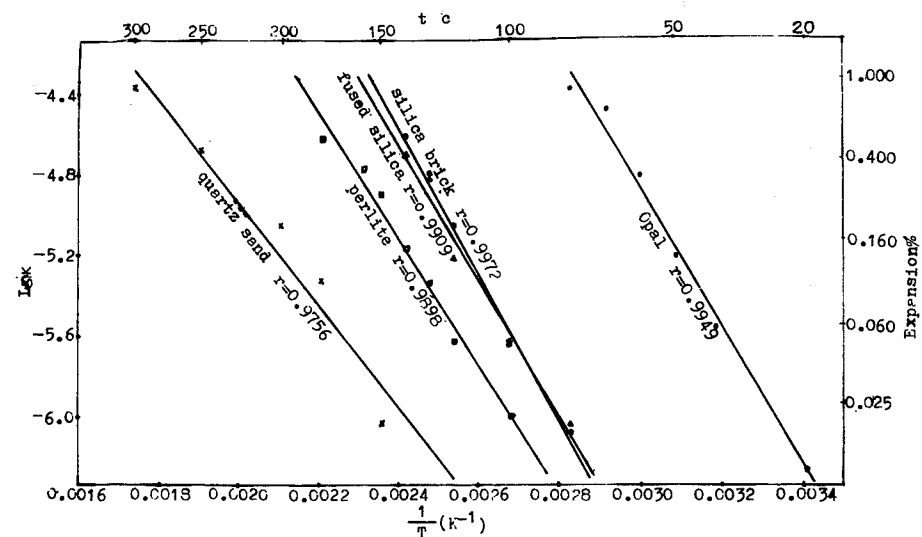


Fig.4 Relationship between lg K and 1/T

Table I E and K_0 of Various Aggregates

| Type of Aggregate | lg K_0 | K_0 | E(Kj/Mol) | Coefficient of Correlation |
|-------------------|----------|--------------------|-----------|----------------------------|
| Opal | 5.32 | 2.09×10^5 | 65.024 | 0.9949 |
| Silica Brick | 4.30 | 1.20×10^4 | 70.500 | 0.9972 |
| Fused Silica | 3.40 | 2.51×10^3 | 64.200 | 0.9909 |
| Perlite | 2.33 | 2.13×10^2 | 59.375 | 0.9898 |
| Quartz Sand | 0.14 | 1.38×10^0 | 48.538 | 0.9756 |

The calculated results show that the differences in activation energy between aggregates are not great, but the differences in frequency factor are obvious. The order of values of frequency factor is:

opal > silica brick > fused silica > perlite > quartz sand

This means that the disordered structure of reactive aggregates is easy to react with the OH^- , K^+ and Na^+ ions. However, it is difficult to explain why the value of activation energy of quartz is the lowest one.

If we have determined a number of K_0 and E values of any aggregates, we can use them to distinguish a reactive aggregate from a non-reactive one. We believe that this would be much better than to identify the alkali reactivity of an aggregate only by the value of expansion of mortar bars cured at a fixed temperature (e.g. 38°C).

The test mentioned above was limited only to alkali-silica reaction. We are going to investigate the behaviour of reactive dolomitic and phyllosilicate aggregates with the same method to see whether it is applicable to them or not.

Finally, we have to say that the alkali-silica reactions are very complex, and they may be kinetically different under different conditions, for instance, with different sizes of aggregates, the dependence of reaction rate on time or on temperature might be different to a certain degree.

4. CONCLUSIONS

(1) According to the dependence of rate of alkali-silica reaction on time, this reaction is in agreement with a pseudo-zero-order rate law.

(2) The temperature dependence of alkali-silica reaction is well in agreement with Arrhenius equation. The value of activation energy E and frequency factor K_0 might be used to identify the alkali reactivity of aggregates. This might be much better than to identify it by the value of expansion of mortar bar cured at a fixed temperature.

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