

Figure 3: The change in weight of the concrete cylinders in relation to the corresponding expansion at any time measured. The straight line shown is found by regression analysis.

does not explain why reinforced concrete when reactive is showing less expansion in practice than found by the tests here carried out.

#### 8. FUTURE TESTS

New tests are planned to give a follow-up and a better understanding of the mechanism of alkali silica reactions in concrete when non-reactive as well as reactive coarse aggregates are used. Furthermore, it is planned in the near future to study the effect of reinforcement on the expansion of concrete due to alkali silica reactions.

## STUDIES OF ALKALI-SILICA REACTION WITH SPECIAL REFERENCE TO PREVENTION OF DAMAGE TO CONCRETE

### A PRELIMINARY STUDY

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#### 1. ABSTRACT

From petrographic studies of alkali-silica reaction damaged concrete specimens and other investigations it has been proposed that the presence of free  $\text{Ca(OH)}_2$  is a necessary pre-requisite for the development of destructive alkali-silica reaction. It has also been proposed that a complete removal of free  $\text{Ca(OH)}_2$ , by reacting with an active pozzolana, will effectively stop the development of destructive alkali-silica reaction, even in the presence of an unlimited supply of alkali-salts. This paper describes work done to test the above hypothesis.

In this work ordinary Portland cement was mixed with different proportions of diatomaceous earth (moler). Using these cement-pozzolana mixtures, 1:3::"cement":sand, mortars were made with each of two known reactive sands and one nearly unreactive sand. 40x40x160 mm. prisms were made from above mortars. These prisms, after 27 days water curing, were tested for their expansivity by hot NaCl bath method.

The observations, to date, indicate that an addition of 20% diatomaceous earth seems to stop expansion due to alkali-silica reaction, even though the prisms were stored in a saturated NaCl bath. A petrographic examination of a thin section of each of the expansion tested prisms failed to reveal the presence of crystalline  $\text{Ca(OH)}_2$  in bars made with "cement" containing 20% diatomaceous earth.

## 2. INTRODUCTION

2.1 From recent reports it will appear that alkali-reactive aggregates are much more widely distributed than was once thought. Their presence have been reported in some countries which were previously thought to be free of them. This wide-spread reporting is partly due to the economic necessity of using second-best quality aggregates and to the increasingly fuel-saving practices of the cement plants which in their turn have lead to raising the alkali contents of cement.

2.2 It is not expected that the above causative factors will change in the near future. It is therefore necessary to find ways and means of preventing the development of destructive alkali-silica reaction. Until now the main emphasis has been on the use of low-alkali cement. However, it has been pointed out that even if low-alkali cement is used, the internal migration and concentration of alkalies may start the destructive alkali-silica reaction. This situation will be much aggravated if alkali-salts migrate from external sources such as sea-water, deicing salts etc.; in such cases the use of low-alkali cement will be of very little use (1). It had also been suggested that the addition of a reactive pozzolana will stop alkali-silica reaction. The amount of pozzolana to be added has to be found empirically. The rationale behind the above suggestion was that the reaction products of the pozzolana and  $\text{Ca(OH)}_2$  would somehow immobilize the limited amount of alkalies present in the cement before it could react with the reactive aggregates of the concrete structure and thereby avoid any damage. Note however, that in cases of structures connected to an unlimited source of alkali-salts e.g. sea-water, the above mentioned protection is expected to breakdown.

2.3 From a petrographic study of concrete specimens damaged by alkali-silica reaction and other investigations it has recently been suggested that the presence of free  $\text{Ca(OH)}_2$  is a necessary pre-requisite for the development of the destructive alkali-silica reaction (2). It has also been proposed that the complete removal of free  $\text{Ca(OH)}_2$  will effectively stop the development of the destructive alkali-silica reaction even in the presence of an unlimited supply of alkali-salts.

2.4 One of the feasible ways of removing free  $\text{Ca(OH)}_2$  from cement paste or concrete is to add a sufficient amount of a reactive pozzolana. According to the above proposal, only the cement-pozzolana mixes which have no free  $\text{Ca(OH)}_2$  will fail to develop the destructive alkali-silica reaction. However, those cement-pozzolana mixes which have free  $\text{Ca(OH)}_2$  will develop the destructive alkali-silica reaction. This paper describes work done to test the above proposal.

## 3. MATERIALS AND EXPERIMENTAL TECHNIQUES

3.1 Sand from three different sources have been used in this investigation. True and Nymølle sand are from land based quarries. The third sand (CN sand) is a sea-dredged one. 0/4 mm. fraction of each of the above sand types were used.

3.2 A single batch of an ordinary Portland cement of Danish origin was used.

3.3 Diatomaceous earth of Danish origin (moler) was used as the reactive pozzolana. This was used without any heat treatment, but was ground to cement fineness.

3.4 In this work the Portland cement was mixed with different proportions of the moler. Using these cement-moler mixes, 1:3::"cement":sand mortars were made from each of the sand types. In each case the water/"cement" ratio was 0.5. Standard 40x40x160 mm. prisms were cast from the mortars. The prisms were cast in such a way that each prism had two length-measuring studs at the centres of the 40x40 mm. faces. These prisms were humid cured for the first 24 hours and then water cured for 27 days. The prisms were afterwards tested for their expansivity due to alkali-silica reaction by means of the hot NaCl bath method (3).

3.5 After eight weeks in NaCl bath, one prism from each mix of each type of sand was removed for petrographic and x-ray diffraction investigations. A part of each prism was used to make thin optical section for petrographic study. The other part was lightly ground and sieved through a 150  $\mu\text{m}$  sieve. The fractions passing through the sieve were used to take x-ray diffraction diagrams in a Guinier focusing camera using  $\text{Cu K}\alpha$  radiation. The individual sand samples were also petrographically examined.

## 4. RESULTS AND DISCUSSIONS

4.1 The petrographic examination of the sand type revealed that:

- a) the sand from True contains a significant amount of opaline flint as the reactive material. It is also poor in limestone content.
- b) the sand from Nymølle contains a significant amount of opaline limestone as the reactive material. It also contains about 20% limestone.
- c) CN sand contains a small amount of macroporous chalcedony. It is poor in limestone.

From the above petrographic results it will appear that the first two sand types will be very reactive as they contain opaline silica as the reactive constituent. If the conditions are drastic enough to make chalcedony to react, then CN sand may also cause expansion.

4.2 The length change measurements are shown in Figs. 1, 2 and 3. It is obvious that True and Nymølle sand form one group and CN sand forms another group. The results will be discussed accordingly.

4.2.1 CN sand: The mortar prisms made with this sand, without any addition of moler, showed no significant length change up to 8 weeks (Fig. 1). The addition of moler caused a small reduction in length even though the prisms were under NaCl solution i.e. there was no possibility of any external drying shrinkage. The above reduction in length increased with increasing moler addition. The reduction in length may be explained in the following way. The reaction

products of moler and  $\text{Ca(OH)}_2$ , which forms in the presence of NaCl, somehow reduce the water permeability of the prisms. The hydration of cement and the reaction of moler with  $\text{Ca(OH)}_2$  continue causing thereby an inner shortage of water and shrinkage.

4.2.2 True and Nymølle sand: The mortar prisms made with these, with out any addition of moler, showed large expansions (Figs. 2 and 3). These rates of expansion confirm the expectations from the petrographic examinations. An addition of moler to the extent of 10% on the weight of cement did not stop the expansion though it delayed the onset and the rate. An addition of 20% or more moler stopped expansion; even caused a little shrinkage to occur. To date there is no indication that expansion will commence at a future date, though the expansion measurement is continuing.

4.3 The petrographic examinations of the thin section of mortars showed that (i) the prisms containing 0 and 10% moler contained significant amounts of crystalline  $\text{Ca(OH)}_2$  (portlandite); (ii) the prisms containing 20 and 25% moler fail to reveal any crystalline  $\text{Ca(OH)}_2$  in them.

4.4 The x-ray diffraction results also showed that the prisms containing 10% moler had crystalline  $\text{Ca(OH)}_2$  in them, but those containing 20% or more moler had no crystalline  $\text{Ca(OH)}_2$ .

4.5 It will thus appear that the suggestions that the presence of free  $\text{Ca(OH)}_2$  is a pre-requisite for the development of the destructive alkali-silica reaction and that the complete removal of free  $\text{Ca(OH)}_2$  stop expansion which has been corroborated.

If these inferences are substantiated by other workers in this field then it would be possible to determine how much of a given pozzolana will be needed to stop the development of destructive alkali-silica reaction.

4.6 A point to be emphasized is that no claim is made as regards continuation or otherwise of alkali-silica reaction. However it is claimed that no destructive alkali-silica reaction occurs in the absence of free  $\text{Ca(OH)}_2$ .

4.7 Further work is in progress to ascertain if alkali-silica reaction continues or not in the absence of free  $\text{Ca(OH)}_2$  and the mechanism by which free  $\text{Ca(OH)}_2$  initiate the development of destructive alkali-silica reaction. This information may enable other preventive methods to be devised.

#### 5. ACKNOWLEDGEMENT

This work has been supported by a grant (16 - 1943 . B892, K633) from the Danish Council of Scientific and Industrial Research (STVF). The authors would like to thank STVF for their support.

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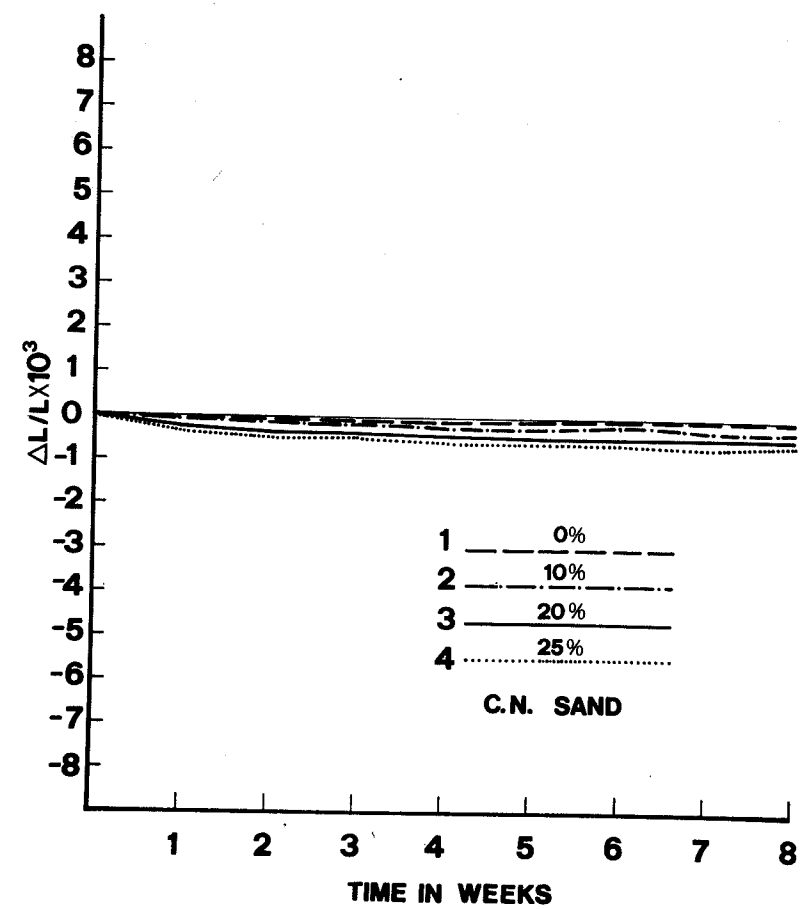


Fig. 1 Time-expansion curves of mortar bars made with CN sand. Figs. in the diagram indicate the % molar content in cements.

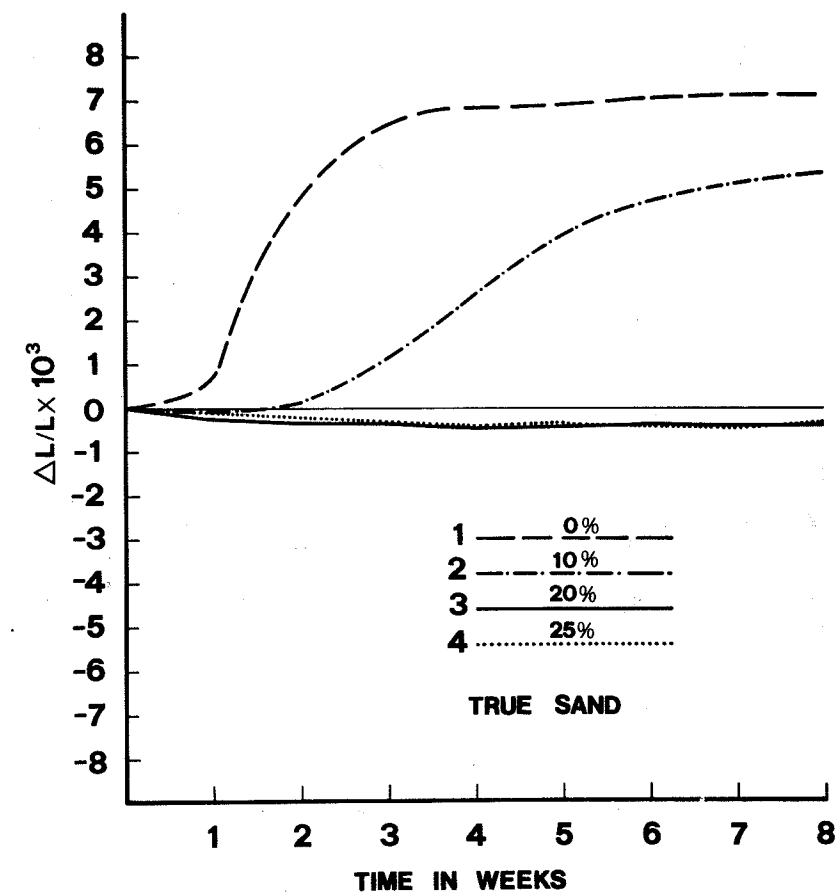


Fig. 2 Time-expansion curves of mortar bars made with True sand. Figs. in the diagram indicate the % molar content in cements.

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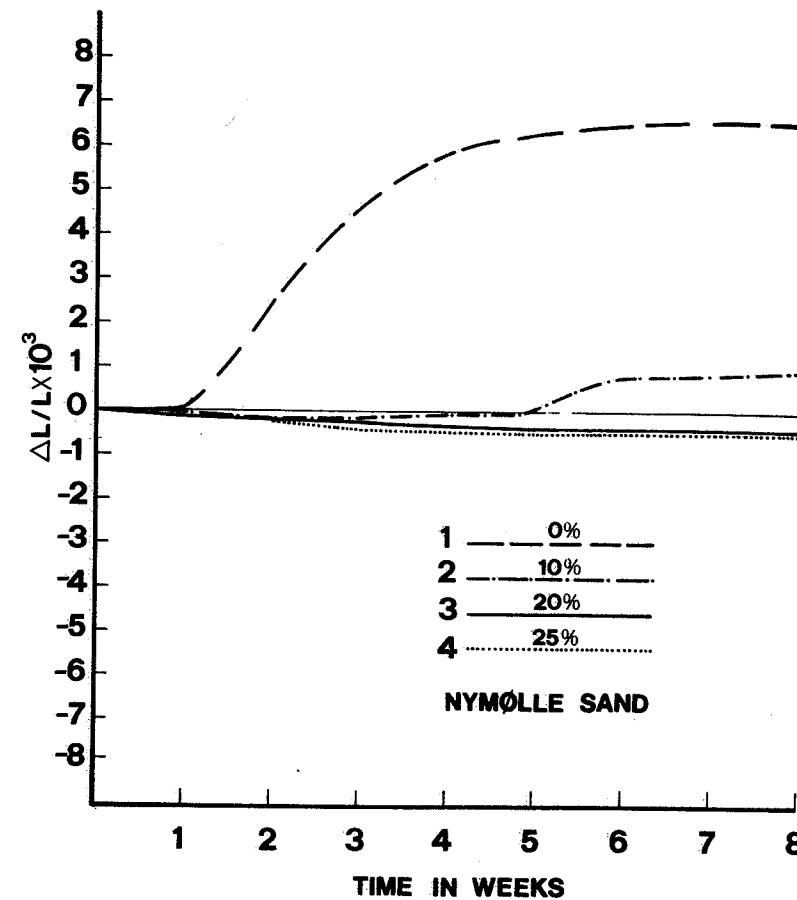


Fig. 3 Time-expansion curves of mortar bars made with Nymølle sand. Figs. in the diagram indicate the % molar content in cements.

## 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.