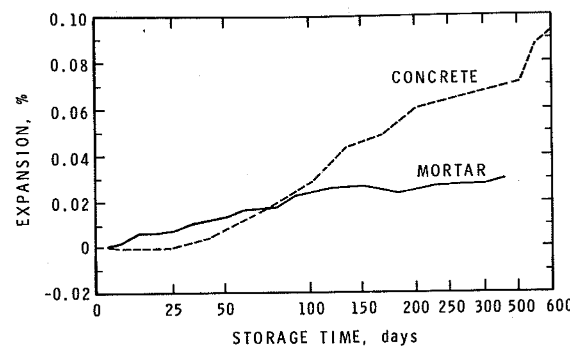


Figure 4 Comparison of expansions of mortar bars and concrete prisms made with greywacke #73-50 from Malay Falls, Nova Scotia /9/, and a cement containing 1.08% alkali

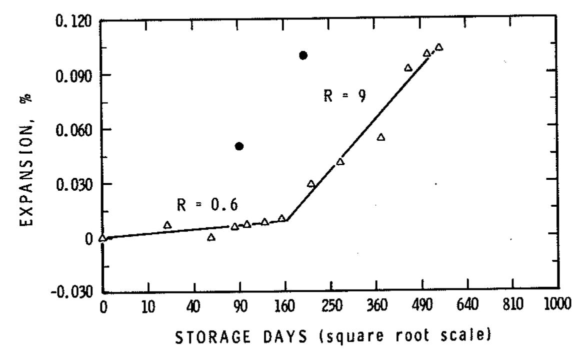
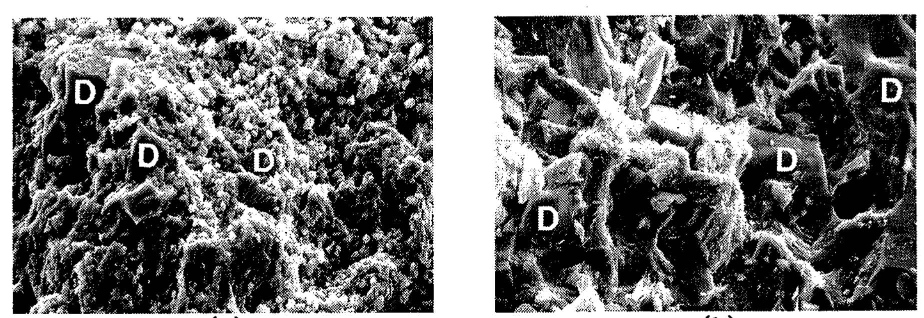


Figure 5 Expansion of mortar bars containing Malmesbury aggregate made with cement containing 0.82% alkalis stored at 38°C and 100% RH.
● - ASTM Limits, R - rate of expansion x 10^3



(a) (b)

Figure 6 SEM micrographs of carbonate rocks from Pittsburg quarry near Kingston, Ontario
(a) Highly expansive dolomitic limestone consisting of isolated dolomite rhombs (D) in a matrix of fine calcite
(b) Non-expansive dolostone consisting of larger dolomite crystals (D) with minor amounts of quartz and calcite

ALKALI-SILICA REACTIVITY OF VARIOUS DANISH FLINT TYPES

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1. ABSTRACT

Measurement of expansivity of sand by the saturated NaCl-bath method in general gives 1 of 4 different expansion characteristics:

I. No expansion

II. No expansion in 8-12 weeks, then slow, but steady expansion over a long period.

III. Initial quick expansion followed by prolonged, slow expansion.

IV. Quick initial expansion followed by an asymptotic expansion.

Thin-section examination shows that the different expansion characteristics could be correlated with different rock types.

Type I occurs when either no reactive particles are present, or only dense, calcedonic flint is present in small amount.

Type II is caused by a somewhat poreous, microcrystalline, calcedonic flint.

Type III occurs in sand types containing small amount of opaline flint and small amount of poreous, microcrystalline calcedonic flint. When the expansion from the opaline flint ceases, the calcedonic flint comes into action.

Type IV occurs when opaline flint is the dominating, reactive rock type.

On the basis of these observations, it appears that most Danish flint types are reactive under appropriate conditions, when salt is added from external sources, but that the rate of reaction is markedly different.

Opaline flint reacts very quickly.

Calcedonic flint reacts slowly, provided it is somewhat poreous.

Dense, calcedonic flint reacts so slowly that the reactivity may be ignored in most practical purposes.

In the design of concrete constructions, the reactivity of the flint should be evaluated and specified using different "reactivity factors" for the different flint types.

2. INTRODUCTION

In Denmark the most common causes of the deterioration of concrete structures are alkali-silica reaction and the freeze-thaw cycles. Recently it has been realized that sand types containing alkali-reactive particles play a very important part in this breakdown. In view of this observation systematic study of Danish sand types has been conducted at the Teknologisk Institut. Some aspects of this investigation have already been published (1, 2, 3). Two different techniques are used in Denmark to evaluate the potential reactivity of sand types. One of these is the warm NaCl-bath technique, a functional technique which estimates the potential expansivity of the sand types under investigation (1). The second is the standard petrographic technique which gives information about the reactive particles, their type, amount, size, distribution, etc. Thus the two methods give related , but not identical information. In this investigation, well over 100 sand types have been studied using both methods to relate their time-expansion characteristics with their mineralogy.

3. MATERIALS AND THE EXPERIMENTAL TECHNIQUES

Sand sources varied from land-based to sea-dredged. The sand types are mainly melt-water deposits from the late-glacial period, though the under sea deposits might have been reworked by currents or wave action. Beside these major sand sources, a few cretaceous and tertiary pure quartz sand types were also included in this investigation.

With each of these sand types 1:3::cement:sand mortar was made. The water/cement ratio of these mortars was 0.5. From each of the mortar mix several 40x 40x160 mm prisms were made. After 27 days water curing the expansivity of these prisms was measured using the warm NaCl-bath method (1).

For the petrographic examination of the sand types, thin optical sections were made either from mortar prisms at the end of the expansion measurements, or from epoxy embedded sand samples. In a supplementary study, Danish flint types were divided into different density ranges and thin-sections made from these fractions were examined. The thin-sections were studied in the optical microscope using polarazing- and fluorescence microscopic technique.

4. RESULTS AND DISCUSSION

4.1 Expansion characteristics of mortar prisms

Expansion upto 1.2% have been measured, although expansion over 0.7% is rare. In general, sea-dredged sand types show less expansion than those from land-based sources. Sea-dredged sand types seldom show expansion exceeding 0.2%.

Expansion-time characteristics are too numerous to be presented individually; however, the expansion-time curves may be divided into four general classes as shown in Fig. 1.

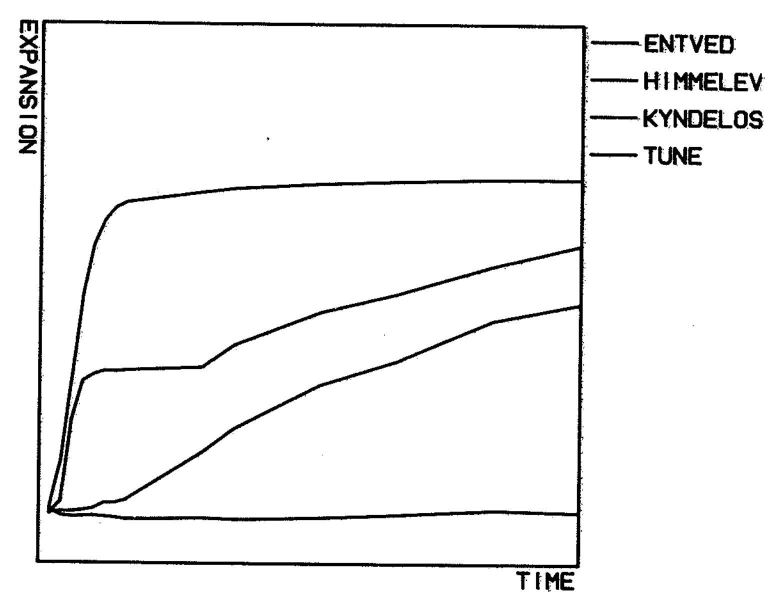

Fig. 1. Shows four general types of time-expansion relationship.

Type I curve, i.e. zero expansion, is generally given by a pure quartz sand; though a few flint-carrying sand specimens from the sea-bed also give Type I curves.

Type II curve is characterized by zero or very little expansion upto 8-12 weeks or more, thereafter there is a slow, but steady expansion over a long period. To date this type of expansion is shown in sand types obtained from sea-bottom or sea beaches, the only exception being a tertiary quartzic sand containing a small amount of reactive materials.

Type III curve is characterized by a high, initial expansion followed by a slow, prolonged expansion. This type is rather rare; only a few marine sand specimens have shown this type of expansion.

The most common type is IV, which is characterized by a high rate of expansion at the beginning, followed by an asymptotic expansion.

4.2 Microscopical investigation of sand types

The thin-sections used in this investigation were about 30x50 mm in size and contained about 3-5000 sand particles. An ordinary point counting technique was used to estimate the fractional volume contents of different rock types in sand samples.

The reactive rock types are easily identifiable in thin-sections of the mortar prisms which were stored in the warm NaCl-bath. Normally, the reactive particles are porous to a varying extent. They often show signs of partial dissolution and internal cracking. Frequently the surrounding cement paste has gel-filled cracks, and devoid of portlandite crystals. After some experience with thin-sections of expanded mortar prisms, it is possible to identify different reactive rock types in thin-sections of the pure sand. Main reactive rock types in sand are different types of flint; the others are opaline siltstones, and rare volcanic rock types from the Scandinavian bed-rock.

4.3 Flint types, their porosity and density

Søndergaard has recognized four different types of flint (4):

a) Calcedonic flint

b) Carbonaceous, calcedonic flint

c) Opaline flint

d) Carbonaceous, opaline flint.

The first two types are usually termed as dense flint and the last two as porous flint.

Dense flint has a characteristic appearance. It can be black brown, grey or white rock with a shiny appearance and has a characteristic conchoidal fracture. The fracture fragments have sharp edges. Microscopically both types of dense flint are dense packing of randomly oriented quartz particles. The incividual quartz grains are below 20 μm in size.

The opaline flint types are white, chalklike material. They are difficult to differentiate visually from limestone. Non-carbonaceous opaline flints are microscopically isotropic except for a few calcedonic inclusions.

Carbonaceous opaline flint types are macroscopically similar to limestone. Microscopically, however, the two rock types are easily differentiable. Individual carbonate grains are smaller in carbonaceous opaline flint than in limestone, and so also the pore size.

Both calcedonic and opaline flint types may contain fossils and, on occasions, a single particle may have both dense and porous parts. Often calcedonic flint grains enclose opaline areas or have an opaline crust. Opaline flint grains nearly always contain inclusions of calcedonic flint particles.

Experience with heavy media density fractionation technique has shown that different types of flints have following densities.

Flint type	Density range in kg/m^3
Calcedonic flint	2595 to 2400
Carbonaceous, calcedonic flint	2595 to 2400
Opaline flint	2200 to 1800
Carbonaceous, opaline flint	2200 to 1800
Calcedonic flint with opaline crust	2590 to 2200

The above noted density variations reflect variations in porosity. The porosity in a rock grain may be made visible by impregnating it with an epoxy resin in which a fluorescent dye has been dissolved. Fluorescence microscopy of a thin-section made from the impregnated grain shows its porosity. By comparing thin-sections of an unknown grain and those of known standards of similar rock types, it is possible to estimate the porosity and hence density of the unknown grain. In general, the calcedonic flint types are non-porous. Porous varieties of calcedonic flint types exist and their porosity becomes visible if density falls below 2500. The opaline flint types have low porosity and are fairly homogeneous except for calcedonic inclusions.

4.4 Expansion and mineralogy of sand types

Since flint grains are the main reactive components in the sand types investigated, it was expected that a relationship may be found between the flint content and expansion. Fig. 2 shows a plot of the total flint content vs expansion of a number of sand types investigated. Fig. 2 shows that the total flint content is not the sole expansion-determining factor. Other factors such as grain size distribution, porosity of the reactive grains, etc. play their part. A detailed comparison of the microscopic and expansion data shows:

i) A Type I expansion curve reflects either flint-free sand or a sand containing calcedonic, microscrystalline flint of high density.

ii) A Type II expansion curve reflects the presence of porous varieties of calcedonic flint or a mixture of small amount of opaline flint mixed with larger amount of calcedonic flint.

iii) A Type III or Type IV expansion reflects the presence of opaline flint grains. The slowly expanding part of the Type III curve may be due to the reactivity of porous, calcedonic flint grains.

5. CONCLUSIONS

i) Under appropriate conditions the flint grains present in Danish sand types can give rise to expansive alkali-silica reaction. The reaction rate varies with the flint type.

ii) Dense calcedonic flint types have the lowest reaction rate. The opaline flint types have highest reaction rate. Calcedonic flint types with opaline crusts com in between.

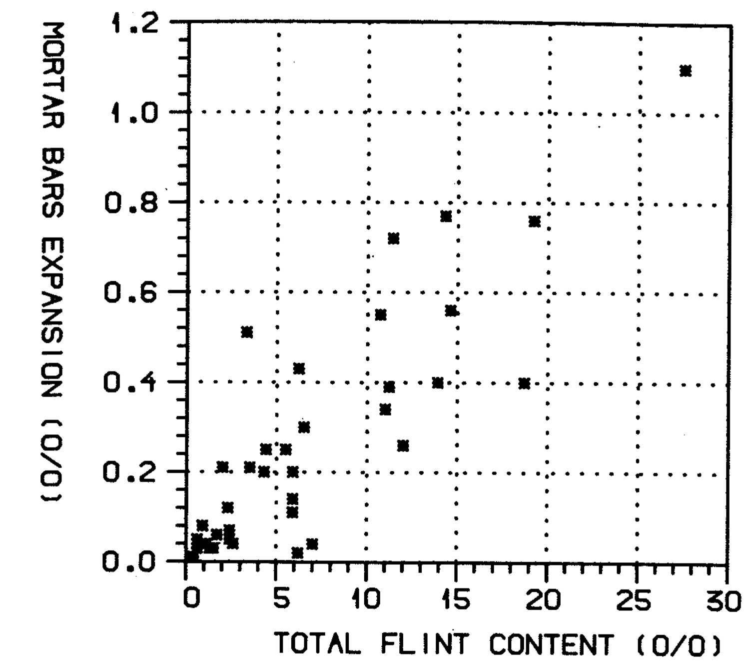

Fig. 2. Shows the relationship between the total flint content and expansion.

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