A Continuous, Quick Chemical Method
for the Characterization of the Alkali-Silica Reactivity
of Aggregates

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ABSTRACT

The system: reactive sand in concentrated alkaline solution is found to experience a volume contraction (chemical shrinkage) as a result of the dissolution of silica. This chemical shrinkage is easily measured by confining the system to a container equiped with a pipette. On the basis of this discovery a quick, chemical method of testing the reactivity of sands has been developed. Due to the accelerated and continuous nature of the measurements complete reaction-curves have been obtained and the effect of various factors influencing the rate of the alkali-silica reaction has been studied. These factors include the effect of porosity, crystallinity, particle size, concentration and kind of alkalies and temperature. Only the major results of these investigations will be reported in this paper.

INTRODUCTION AND THEORETICAL

Quantitative assessment of the alkali-silica reaction in mortar or concrete is extremely difficult because of the influence of the complex chemical and physical nature of the cement paste. The only quantitative means available so far for following the alkali-silica reaction in these systems is to measure the expansion resulting from the reaction. Since the expansion behavior of the alkali-silica reaction depends on various factors like the porosity of the specimen, availability of water, temperature etc. the measurement of expansion may be of doubtful value in establishing the state reached by the reaction itself.

In systems of greater simplicity, i.e. systems consisting of only silica in alkaline solutions, the reaction may be followed quite accurately by a diversity of well-established methods of analysis, perhaps the most direct being the chemical analysis determining the amount of silica dissolved as a function of time. In such "pure" systems the rate of reaction may furthermore be controlled by varying for instance pH and temperature, and so possibly achieving highly accelerated alkali-silica reactions. These "laboratory models" of alkali-silica reactions may be considered poor replicas of what is going on in concrete, but for the sake of determining differences in the reactivity of sands and to reveal the factors influencing the rate of the reactions, these systems serve an important purpose in characterizing aggregate reactivity. Whether the results of highly accelerated methods can be translated quantitatively to concrete practice depends of course on the result of comparison with other more realistic and less accelerated methods, as has been done for instance in the comparison of the results of the quick chemical test ASTM C 289 with those of the mortar-bar expansion method ASTM C 227.

When using the chemical shrinkage method to monitor alkali-silica reaction, sand sized material is put in 10 molar NaOH solution at 5o°C and the volume contraction is monitored. The apparent contradiction between the contraction of the total system silica + NaOH and the expansion forces generated by reactive silica in concrete can be understood by comparing it to the system cement + water, in which the total volume of the system decreases while the volume of solids increases. In the case of the alkali-silica reaction the availability of water from outside the system permits the silica gel to absorb water and create a swelling pressure which more than compensates for the deficit in water resulting from the reaction itself.

EXPERIMENTAL

Preparation of sands and methods of measurement.

Sands were tested in a water-saturated state in the fractions 4-2 mm, 2-1 mm and 1-o.3 mm. Saturation was achieved by evacuation under (boiled) water for about 3 hours with 25 g of each sandfraction placed in 5o ml flasks, each containing sufficient water to avoid drying due to the evaporation. To secure effective elimination of the air contained in the sands, evaporation was kept steady and lively by vibrating the evacuation vessel (containing several flasks). This vibration was accomplished by placing the vessel on the vibrating table ordinarily used for sieving purposes.

After evacuation, water was decanted from the flasks and exchanged with lo molar sodium hydroxide by repeated mixing and decanting. Finally the flasks were filled to the top with paraffin oil resting on top of the sodium hydroxide solution, and the flasks were fitted with a o.2 ml pipette. The filling of the flasks with paraffin oil was done to avoid contact with the highly aggressive sodium hydroxide solution. The flasks containing the sand fractions covered with lo molar sodium hydroxide were deposited in a 5o°C thermostatic bath. Thermal equilibrium was obtained within 2o min and the oil-miniscus in the pipette started sinking as a result of the chemical shrinkage of the reacting system, and recording was commenced.

Because of the expected slight dissolution of the inner surface of the glass-flasks long term measurements require comparison to blind-samples not containing reactive sands.

Repeated measurements (3-5 times on 3 different sands) gave an average relative error of approximately lo% when the chemical shrinkage was measured after 2o hours.

The continuous nature of the measurement of chemical shrinkage lends itself to automization. Recently the Konometer has been developed in Denmark to accomplish automatic measurements of chemical shrinkage of hydrating cements and for testing sand (see Fig. 1). As mentioned in a recent publication, other reactive materials relevant to the cement and concrete industry, such as flyash and microsilica, etc. can be characterized by the same general method of measurement (Knudsen 1985).

RESULTS AND DISCUSSION

Correlation to dissolved silica.

In order to verify that the observed chemical shrinkage of the system: reactive sand plus lo molar sodium hydroxide is actually the result of the dissolution of the silica, a danish white flint, containing large amounts of opal, was crushed and tested both by chemical shrinkage and by analysis of dissolved silica (by the gravimetric method). Figure 2 shows the correlation between chemical shrinkage due to the reaction and the amount of silica going into solu-

tion. In a similar experiment with crushed dense chalcedonic flint, in which
the reaction is thirty times slower than with opal, there is also a correlati-
on between chemical shrinkage and the amount of dissolved silica, except that
in this case the relationship is not linear. This lack of linearity is ascribed
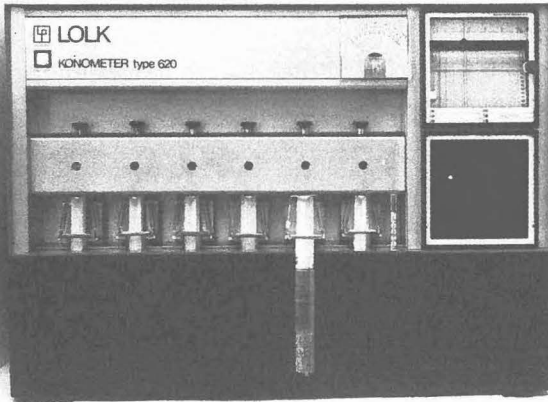to the experimental difficulty of eliminating all the absorbed air in the dense
flints.

Fig. 1. The Konometer Type 62o automatically measures the chemical shrinkage
        of 6 samples simultaneously. The sample-holder used when testing sands
        is shown in front of the thermostatic bath in the bottom of the Kono-
        meter.

Correlation to mortar-bar expansion.

        An accelerated mortar-bar expansion method designated TI-B51 (Chatterji,
1978), has been the common method in use for some years now as a standard test
of alkali-reactivity of Danish sands. Typical results of expansion test ac-
cording to this method show two stages in the reaction. The first starts a few
weeks after initiation of measurement and levels off at lo-2o weeks when the
second starts, this levels off only after 5o-loo weeks. When sands have been
subjected to test by measuring chemical shrinkage the same pattern is seen to
emerge, except the time-scale is now hours instead of weeks!

        In TI-B51 a limit of acceptance has been placed at o.1% expansion after
8 weeks, which means that sands containing only the second stage are normally
accepted in spite of the fact that the second stage of expansion may lead to
larger levels of total expansion than the first. When the limits set in TI-B51
are translated to the much faster chemical shrinkage method (faster due to the
high alkali concentration) they are: o.4 ml shrinkage/kg sand after 2o hours.
2o Danish sands, varying significantly in reactivity have been tested by the
two methods and the results are given in Fig. 3. It can be seen, that the two
methods agree on accepting 5 of these sands, and rejecting 14. One particular
sand was rejected by TI-B51 and accepted by the chemical shrinkage method. A
later test on the Konometer placed this point in the mutual rejection-zone of
the two methods! Thus the two methods seem to be equivalent in their state-
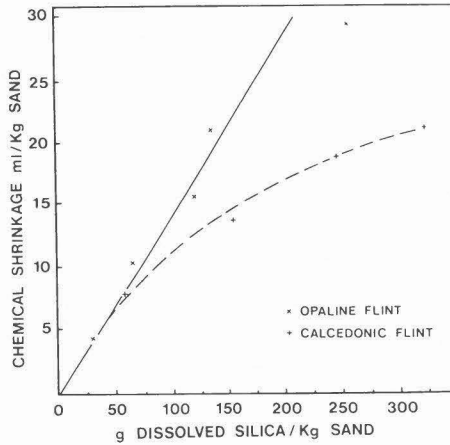ments regarding alkali-reactivity of sands.

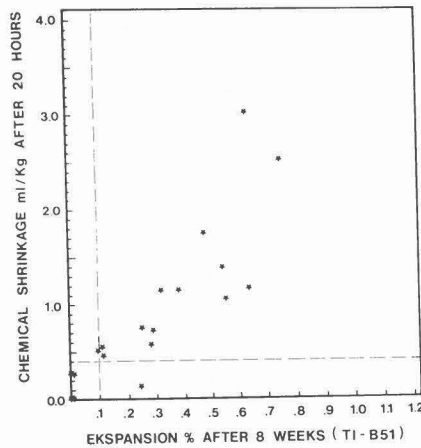Fig. 2. The relationship between chemical shrinkage and dissolved silica for an opaline and calcedonic flint.

Fig. 3. The results of tests of 2o Danish sands by the expansion method, TI-B51, and by the chemical shrinkage method.

Continuous measurement of the alkali-silica reaction.

Besides offering the advantage of very quick testing, the chemical shrinkage method offers the possibility of continuous measurements. This capability has been highly beneficial in our various investigations of factors influencing the rate of the alkali-silica reaction. The factors we have investigated are: the influence of temperature, of concentration of alkali hydroxide, of the kind of alkali-ion, of the fraction of sand and the effect of particle size on the rate of reaction.

Identification of reactive phases.

An important use of the chemical shrinkage method, which depends on its ability for continuous monitoring of the alkali-silica reaction, consists of a detailed comparison of (total) reaction-curves with the aim of identifying reactive phases in natural sands. A density fraction (heavy-liquid separation) <2.3 g/cm^3 of a Danish land-dredged sand was compared to Beltane opal. The pattern of reaction was almost identical for the two materials, and the identification of this low-density fraction as opal was justified. From a mineralogical point of view differences may exist, as for instance revealed by microscopy, and these differences could otherwise give rise to speculations of differences in reactivity. The strength of the chemical shrinkage method, is that the importance of chemical or physical differences may quickly be checked and their significance from a reaction point of view revealed.

Another example was the same density-fraction of a sea-dredged sand which was compared to a sample of dense, black flint from Stevns. Again a significant similarity in reaction patterns was observed, but this time the reaction took about 5oo hours to complete, compared to about 5 hours for the opaline flint.

A very interesting point emerges from these findings, which has an important impact on the result of petrographic, investigations of sands. Porosity, as determined in thin-slices of samples of sand, has generally been considered a major parameter in judging reactivity. Findings with the chemical shrinkage method, and verified by mortar-bar expansions (TI-B51) (3), shows porosity to be of insignificant importance compared to differences in crystallinity. A low density when associated with an opaline substance gives rise to almost 1oo times the reaction rate of a crystalline calcedonic flint with the same density!

CONCLUSIONS

Measurements of the chemical shrinkage accompanying alkali-silica reactions have been used in testing of the reactivity of sands. With the highly reactive systems (sand + lo molar Sodium hydroxide at 5o^{o}C) used in our investigations this method offers the opportunity of measuring total reaction-curves in a matter of days. The results can be used for scientific investigation and for quality control of sands. When used for testing sands, the method gives similar results to the 8-weeks expansion test (TI-B51), but in one day! In its more general use it offers the possibility of obtaining continuous reaction-curves and may be used in evaluation of the effect of various factors on the rate of the reaction. The major experimental difficulty in applying the method lies in the preparation of complete water-saturated samples of sands prior to testing.

REFERENCE LIST

1. Knudsen, T., Cement and Concrete Research 15:72o (1985).

2. Chatterji, S., Cement and Concrete Research 8:647-650 (1978).

3. Private communication with the Technological Institute, Tåstrup.