

THE CHEMICAL SHRINKAGE TEST; SOME COROLLARIES

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Results from an inter-laboratory test in Denmark in 1990 are presented. Proportionality was demonstrated between the content of reactive material and the amount of chemical shrinkage measured. With the coarsest fraction, 2-4 mm, the measured standard deviation was dominated by fluctuations in the number of reactive grains. Assumption of a Poisson distribution was in good agreement with measurements. The contents of opaline flint in the 1-2 and 2-4 mm fractions in Danish sands, seem to be in constant proportion.

INTRODUCTION

The chemical shrinkage method, performed on the automatic Konometer (TK-84), can be considered a quick chemical test of the reactivity of sands. Its continuous monitoring of the extent of reaction, and the determination of the content of reactive material, is leaning on the measurement of the negative change of volume, accompanying the dissolution of reactive silica in concentrated alkali hydroxide (10 molar NaOH, 50°C). The use of the term shrinkage in connection with a test method on expanding aggregates is explained by the fact, that chemical shrinkage measurements are carried out on closed systems, whereas measurements of expansion are carried out on open systems, that are allowed to absorb water from the surroundings. Many chemical reactions are accompanied by negative changes of volume, as exemplified by the hydration process of cement.

The chemical shrinkage test was developed at the Institute of Mineral Industry (1984-1985) in a project supported by Cowi-consult, a Danish engineering firm. Later the method was extended and improved in a project conducted by the Danish Road Directory in co-operation with the Danish Technological Institute (1988-1990), financially supported by Cowi-consult.

The chemical shrinkage method was reported for the first time at the 7th International Conference in Ottawa, 1986 (Knudsen (1)) where the principal elements of the method was presented. Later, at the 8th International Conference in Kyoto, 1989, the detailed procedure of the measurement performed with the Konometer was demonstrated at a poster-session (Knudsen & Eriksen (2)).

In 1988 the method was accepted for testing sand by the Basic Concrete Specification of Building Structures. By their recommendations the limit for acceptance of sands to be used in concrete exposed to moderate and aggressive environment was set to 0.30 ml of chemical shrinkage per Kg of sand.

Today, the method has been adapted by several laboratories in Denmark, and numerous tests by this method has been performed.

In 1990 an inter-laboratory test involving 8 different laboratories was conducted, demonstrating the reproducibility of the method. Results from this test will be reported here.

In this paper the proportionality between the contents of reactive material and the amount of chemical shrinkage will be demonstrated. An evaluation of the influence of sample-size on the error of measurement will be given. Finally the constant proportion of the contents of reactive material in the 1-2 mm and the 2-4 mm fractions in Danish sands will be demonstrated.

EXPERIMENTAL AND DISCUSSION

Inter-laboratory test with TK-84 in Denmark, 1990

A Danish sand of low reactivity was sent to 8 laboratories in Denmark as part of a ring-test with the chemical shrinkage method TK-84. The results collected from the 8 laboratories are presented in table 1. The average of chemical shrinkage in each fraction can be seen in column 3, and the individual results from the laboratories are illustrated in figure 2. The means of the contributions from each fraction to the chemical shrinkage of the sand are seen in column 4, and illustrated in figure 1. (Labs. A and C found nil in the finest fraction).

A Poisson distribution was used to simulate the effect of sampling. Sample sizes in the TK-84 are 112 grams of each fraction, and it was expected, that the effect of sample size would show up in the coarsest fraction 2-4mm, due to the limited number of reactive grains in this fraction. The results of this calculation is shown in column 5 in tabel 1, given as relative errors.

TABLE 1 - The Results from the Inter-Laboratory test with Averages of the Results from 8 Laboratories.

Fract. size (mm)	Fract. part (%)	ml/Kg Fraction	ml/Kg Sand	Rel. Err. Poisson	Rel. Err. found
0.5-1	24.0	0.13	0.031	0.06	0.85
1-2	13.5	0.49	0.067	0.09	0.29
2-4	11.8	0.89	0.105	0.20	0.18
0-4	100	0.20	0.203	0.11	0.27

For comparison, the relative errors found by collecting the results from the 8 laboratories are shown in column 6. As expected, the coarsest fraction is dominated by sampling errors (the value calculated on assuming a Poisson distribution is even a little greater than the value actually found!). For the finer fractions other errors than sampling errors are dominating, and a lot larger than the latter. A doubling of runs of the 2-4 mm fraction would only result in reduction of the experimental relative error from 0.27 to approximately 0.21, due to the significant contribution of errors from the finer fractions.

The sample sizes, 112 grams for each fraction in a TK-84 test, consist of two separate samples of 56 g each. The large deviation sometimes experienced with the 2-4 mm fraction, between these two separate test samples, can be rationalized on the ground of the large contribution of sampling errors for this coarse fraction.

The results of the test samples of 56 grams were used to take a close-up look at the agreement with the Poisson distribution. Further runs were made in our laboratory, resulting in a total of 24 separate tests of 56 grams of the 2-4 mm fraction. The result of this comparison with the Poisson distribution can be seen in figure 3. In calculation of the number of reactive grains in the test sample the assumption of a constant frequency of grain sizes within each size class was used in order to calculate a mean size. A specific gravity of the opaline flint grains of 2.1 Kg/l was assumed to give a mean mass of reactive grains in the 2-4 mm fractions. Since the specific chemical shrinkage of opaline flint (Goettrup) has been found to be 64 ml/Kg the number of reactive grains corresponding to the chemical shrinkage read for each of the 24 samples could be calculated. A mean of 13 reactive grains was found as seen on figure 3. The good agreement between theory and experiment seen in this figure is taken as an indication of the validity of the assumption, that the opaline flint occurs as grains consisting of only opaline flint.

Chemical Shrinkage as an Indicator of the Amount of reactive Flint

The chemical shrinkage method was presented at the international meeting in Ottawa 1986 (1). The method was shown to correlate linearly with 8 weeks expansion (TI-B51) and with dissolved silica. The linear correlation with the expansion test was demonstrated with a limited number of samples. Since then, the correlation has been shown with a much larger number of samples. One laboratory, for instance, routinely engaged with sand tests, found 80 out of 88 to comply with the acceptance criteria of both methods, thus demonstrating the close correlation between the two.

The correlation between the content of reactive aggregate and the amount of chemical shrinkage has not been presented until now.

A total of 62 synthetic sands were made by mixing of Goettrup flint with an inert sand. Weight percentages were in the range 0-6, corresponding to a chemical shrinkage from 0 to approximately 4 ml/Kg of synthetic sand. Two fractions were run, the 0.5-1

and the 1-2 mm fractions. The results are shown in figure 4, as the reading of chemical shrinkage from one sample-holder (56 g). From the linear correlation of results, a specific shrinkage for Goettrup flint of 64 ml/Kg can be derived. In fig.2 of reference (1) a value of approximately 140 ml/Kg of dissolved silica is seemingly contradicting the 64 ml/Kg found in the present investigation!

There are two reasons for this apparent discrepancy. One, the dissolution taking place in the densely packed sample-holder is one with local fluctuations of concentrations, due to the absence of stirring. The silicates formed by the dissolution may therefore deviate from what is found under conditions more approaching equilibrium.

This was investigated by using glass flasks as containers, and a larger proportion of sodium hydroxide to silica. Furthermore the reactants were kept continuously stirred. Three independent runs gave a value of approximately 90 ml/kg of reactive flint. The effect of stirring could easily be verified, by stopping for some time and starting the stirring again. This resulted in a rapid rise in the amount of chemical shrinkage, after a leveling off during the period of no stirring.

In these experiments, the Goettrup flint was found not to be completely soluble; a residue of approximately 30 % was found. When we correct for this insoluble part of the reactive flint, we get a value of ca. 130 ml/kg of flint dissolved. This value agrees well with the value stated earlier from Ref. (1), of 140 ml/Kg dissolved silica, considering the difficulties of retaining the fine residue on a filter-paper, which results in an underestimation of the amount of residue.

On the Effect of Calcium Carbonate in Danish Sands

If a ground calcium carbonate rock is tested with the chemical shrinkage method, a negative value of the chemical shrinkage is found. The incongruent dissolution of this compound in highly concentrated sodium hydroxide, results in an increase in the volume of the products minus the volume of reactants.

This fact raised for some time the question of whether the content of calcium carbonate particles in Danish sands could possibly lead to errors in the chemical shrinkage method TK-84. As it turned out, this was shown not to be the case, for the following interesting reason. When the sand contains reactive silica the rapid production of silicate ions secures an equally rapid formation of calcium silicate hydrate on the surface of the calcium carbonate grains. This reaction can take place, since the surface of these carbonate grains is transformed into calcium hydroxide at the moment of exposure to the concentrated sodium hydroxide solution. The dense layer of calcium silicate hydrate, as seen in thin sections, stops the dissolution of the calcium carbonate grains.

An experimental verification of the hindrance of the dissolution can be seen in figure 5. In this case the 1-2 mm fraction of

a Swedish sand contained 15% of calcium carbonate, and no reactive silica. The chemical shrinkage read was -0.5 ml/Kg. We mixed this sand fraction with crushed Goettrup flint in proportions 0.25 to 6 % , and measured the chemical shrinkage. The straight linear relationship found, cuts the ordinate axis at zero chemical shrinkage as expected when assuming no influence of the presence of calcium carbonate. Even the measurements with .25 % of reactive flint do not seem to be influenced by the 'latent' negative chemical shrinkage due to the 15 % of calcium carbonate in this sand fraction.

In the TK-84, if negative chemical shrinkage is read, the content of reactive silica in this fraction is being set to zero! The occurrence of negative chemical shrinkage is generally limited to the 0.5-1 mm fractions of sands with a very little content of reactive silica. This is in accordance with the results seen in figures 1 and 2, showing a rapid decline in reactivity through the fractions 2-4, 1-2 and 0.5-1 mm.

Content of reactive Material in the 1-2 and 2-4 mm Fractions in Danish Sands.

Investigations carried out by the Danish Technological Institute (Grelk (3)), applied among other methods of testing the "German method" in order to compare the content of reactive material in the 1-2 and the 2-4 mm fractions. Figure 6 shows the results of their measurements, together with the results of the chemical shrinkage method on other Danish sands. In plotting the results of the German method together with the results of chemical shrinkage, use has been made of the specific shrinkage found for the reactive flint from Goettrup, 64 ml/Kg. The results from chemical shrinkage support their finding of a proportionality between the contents in these two fractions, and further indicate that the specific shrinkage found for this particular reactive flint is common to the opaline flint found in Danish sands.

Besides the possible importance of this finding for workers concerned with explanations of the presence of opaline flint in Danish sands, the reason for the inclusion in this paper, is one of setting the chemical shrinkage method into perspective with other methods of measurement. (The "German method" uses a treatment with 2.8 molar sodium hydroxide in 4 hours at 90°C , of the fractions 1-2 and 2-4 mm. The decrease in weight by sieving, after the treatment with sodium hydroxide, is taken as the amount of reactive flint contained in these fractions).

REFERENCES

1. Knudsen, T., 1986, "A continuous, quick chemical Method for the Characterisation of the Alkali-Silica Reactivity of Aggregates", 7th International Conference, Ottawa, Canada.
2. Knudsen, T., and Eriksen, K., 1989, 8th International Conference, Kyoto, Japan. (Poster, not in Proceedings)
3. Grelk, B., 1985, "Gruskvaliteter", Technological Institute.

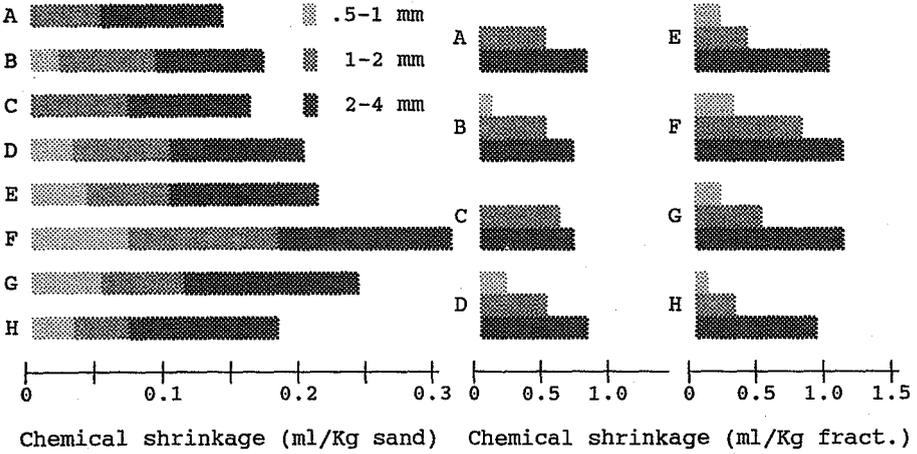


Figure 1 Contributions of each fraction to total shrinkage.

Figure 2 Chemical shrinkage found in each fraction.

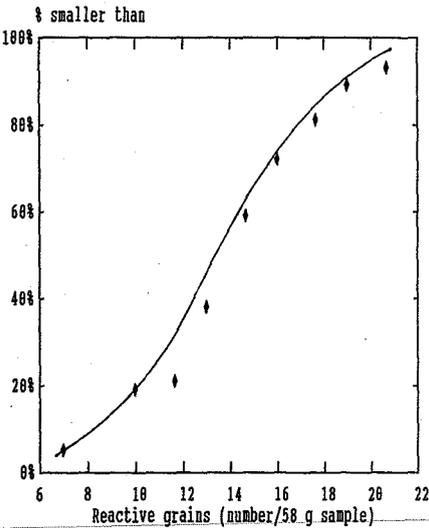


Figure 3 Variation in number of reactive grains. Line: Poisson.

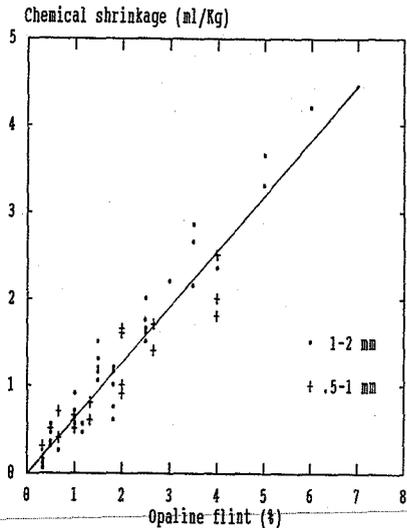


Figure 4 Chemical shrinkage vs. amount of reactive flint.

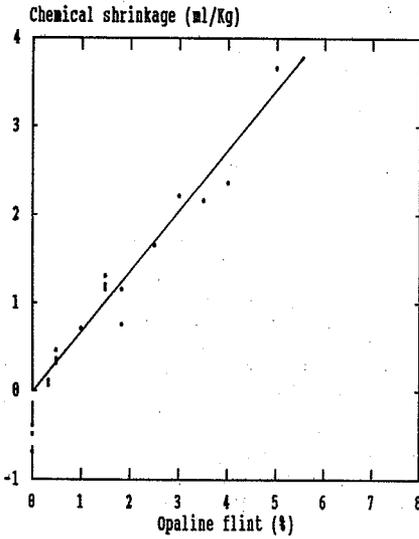


Figure 5 Chemical shrinkage vs. amount of reactive flint.

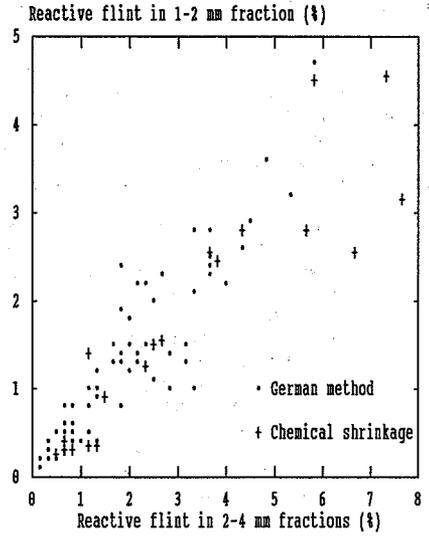


Figure 6 Amount of reactive flint in 1-2 and 2-4 mm fractas.