

INFLUENCE OF THE AMOUNT OF MIXING WATER ON THE ALKALI-SILICA REACTION

by Dr Dennis Lenzner*

SYNOPSIS

The mixing water content of a mortar determines its porosity and the concentration ratios within the pore solution. Both are parameters which influence the alkali-silica reaction and the consequent rate of deterioration.

Some liquefacients added to improve the workability of concrete are alkali salts of organic compounds, and can be expected to have an influence on the alkali silica reaction.

The results of a series of tests with mortar specimens with different w/c-ratios and with the addition of two commercial liquefacients are reported.

SAMEVATTING

Die porieusheid van 'n mortel en die konsentrasieverhoudings in die porie-oplossing word bepaal deur die mengwaterinhoud. Albei is parameters wat die alkali-silikareaksie en die gevolglike tempo van verswakking beïnvloed.

Sommige bewerkbaarheidsmiddels, wat bygevoeg word om die werkbaarheid van beton te verbeter, is alkali-soute van organiese verbindings en daar kan verwag word dat dit die alkali-silikareaksie sal beïnvloed.

Verslag word gelewer oor die resultate van toetse met mortelmonsters met verskillende w/s-verhoudings en met byvoeging van twee bewerkbaarheidsmiddels wat in die handel verkrygbaar is.

S252/26

Conference on alkali-aggregate reaction in concrete
Cape Town - South Africa
March 30 - April 3, 1981

Konferensie oor alkali-aggregaatreaksie in beton
Kaapstad - Suid-Afrika
30 Maart - 3 April, 1981

Secretariat: NBRI of the CSIR
P O Box 395, Pretoria 0001, South Africa
Telephone (012) 86-9211 Telegrams Navorsbou
Telex SA 3-630

Sekretariaat: NBNI van die WNNR
Posbus 395, Pretoria 0001, Suid-Afrika
Telefoon (012) 86-9211 Telegramme Navorsbou
Teleks SA 3-630

* Institut für Gesteinshüttenkunde, RWTH Aachen, Germany

1. FUNDAMENTALS

The alkali-silica reaction (ASR) is not only determined by the kind and the amount of the reagents, which are the alkalis in the cement and the reactive silica in the aggregate, but also by all the other parameters that influence the hardening of the cement in one way or another.

One very important parameter in the field of practical concrete manufacture is the water-cement ratio, which is defined as the mass of mixing water to the mass of cement in the concrete mixture. It is well known that with constant cement content and otherwise equal conditions the amount of mixing water determines the porosity of the hardened cement paste as shown in Figure 1.

Closely correlated with this porosity is the permeability.

As Figure 2 shows, the water permeability of the hardened cement paste increases significantly with the w/c ratio, i.e. the diffusion resistance of the structure decreases, so that that part of the ASR which is diffusion dependant is promoted.

On the other hand, with a higher porosity there is more pore space available for the reaction products formed during the ASR, so that a smaller amount of the swelling pressure is transmitted to the structure.

Furthermore, the ion concentration of the pore solution is inversely proportional to the w/c ratio. Since it can be assumed that the reaction rate depends on the ion concentration of the solution, the ASR will begin more rapidly when the w/c ratio is low.

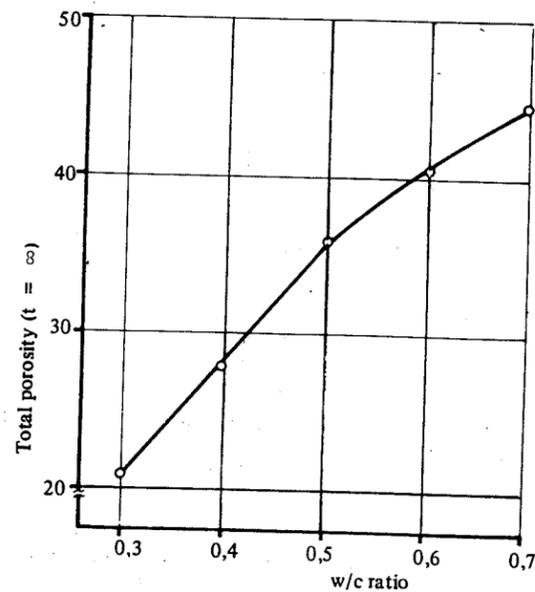


FIGURE 1: Porosity versus w/c ratio after Krogbeumker¹.

Finally, the strength development of the hardened cement paste depends on the w/c ratio, i.e. the lower the w/c ratio the more rapid is the gain in strength under otherwise similar conditions. However the more rapid the strength gain, the smaller the amount of swelling pressure that can be assimilated by the cement while it is still plastic.

The result of these opposing influences from the differing mix-water ratios, is that the maximum damage attributable to the ASR is to be expected at a median, the pessimum, ratio.

2. EXPERIMENTAL

During our investigations of the ASR with opaline sandstone from Schleswig-Holstein, mortar specimens with w/c ratios of 0,4, 0,5, 0,6 and 0,7 were prepared.

The cement had a moderate alkali content of 0,9 per cent m/m Na₂O-equivalent. In preparing the mortar the cement/aggregate ratio was 1/3 and the preparation was according to the German cement standard DIN 1164. The reactive aggregate, an opaline standstone with a grain size of 0,09 - 0,5 mm, was added as a 4 per cent m/m replacement for a standard sand.

In order to determine the initial alkali ion concentration in the mixture, cement pastes were prepared with the same mix proportions. These pastes were centrifuged at the time when the aggregate would have been added to the mixture during normal preparation. The alkali ion concentration of the clear solution was determined by atomic absorption techniques, (see figure 3, page 2).

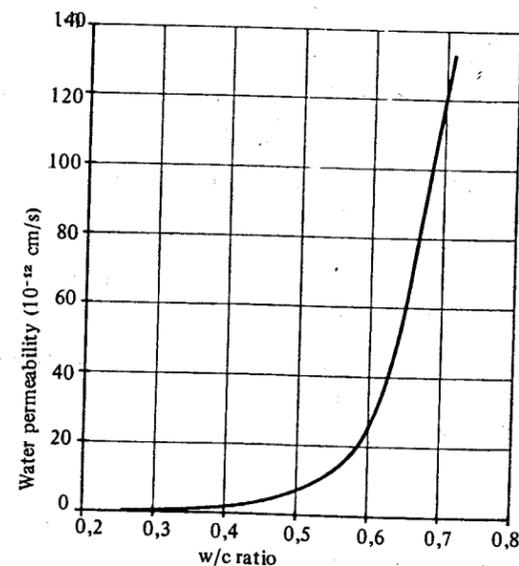


FIGURE 2: Permeability versus w/c ratio after Powers et al².

Plasticisers based on lignin-sulfonate have been well known for a long time. However, the super plasticisers based on artificial resins, which have been developed during recent years, have proved to be more efficient.

Mortar bar tests were carried out with two commercial super plasticisers and with opaline sandstone as the reactive aggregate. Plasticiser A is a condensation product of melamine and formaldehyde while B is made of naphthalene sulfonic acid and formaldehyde.

Both admixtures are alkali salts, which means that they cause a higher alkali concentration in the pore solution.

The initial alkali concentration was determined as described above. The results are given in Table 1.

TABLE 1 : Starting alkali concentration in [mg/m ℓ]

w/c ratio	0,4	0,5	A/0,4	B/0,4	B/0,45
Na ₂ O	0,52	0,42	1,80	1,90	1,67
K ₂ O	16,8	15,1	16,4	15,8	14,6

According to the manufacturers' recommendations, the quantities of A and B were 2 and 1,5 per cent m/m of the cement portion in the mixture respectively. Table 1 shows, that the plasticisers raised the sodium concentration of the solution significantly.

The flow of the mortars is shown in Table 2.

TABLE 2 : Flow of the test mortars in [cm]

w/c ratio	0,5	A/0,45	B/0,45	B/0,40
flow	16,1	16,9	20,0	15,1

It is shown that in spite of a water reduction of 10 per cent the workability of the mortars containing the plasticisers was better than that of the reference mortar.

With these mortars, bars were prepared and stored in the way already described.

The results of the expansion and natural resonance frequency measurements are shown in Figure 5.

It can be clearly seen that the plasticisers accelerate the deterioration significantly. The plasticiser based on naphthalene has a slightly stronger effect than the one based on melamine.

The reason for the acceleration is thought to be the high alkali concentration of the solution.

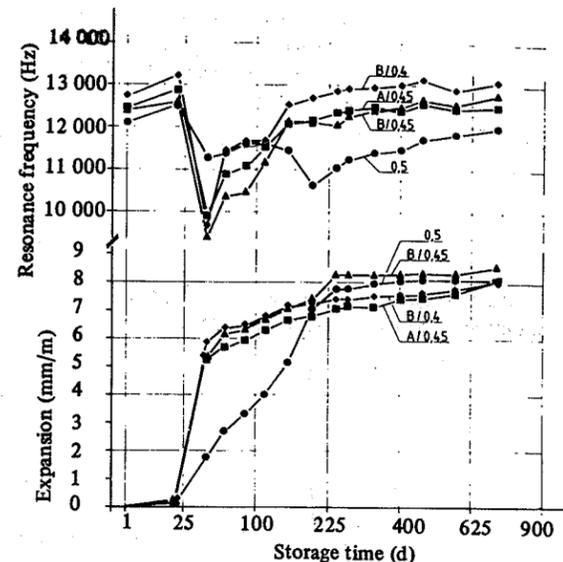


FIGURE 5: Damage caused by the ASR in mortars containing plasticisers.

Following the rapid start to the reaction, the autogenous rehealing begins after about 40 days, as indicated by the increase in the natural resonance frequencies. The deterioration caused by the ASR, however, had not terminated as was shown by the continued expansion and by the natural resonance frequency decrease at intervals.

The natural resonance frequency of the reference specimens increased continuously after 190 days until after about 400 days no further expansion was detected.

On the other hand, the specimens with plasticisers underwent a marked natural resonance frequency decrease even after 450 days and showed increased expansion after about 600 days.

The cause of this lasting reaction might be the attack of less reactive forms of silica in the aggregate by the strongly alkaline pore solution, or the larger quantity of alkali which was set free from the alkali silicates during their reaction with lime.

However, up to a curing period of 600 days, the total deterioration of the reference mortar was greater than the one containing the plasticisers. This agrees well with the observation stated elsewhere², that an acceleration of the ASR causes reduced deterioration.

The reaction will have to be allowed to reach its conclusion in all specimens before the influence of plasticisers on the ASR can be finally determined.

5. CONCLUSION

The tests reveal that ionic plasticisers which release alkalis to the solution significantly accelerate the ASR. After rapid

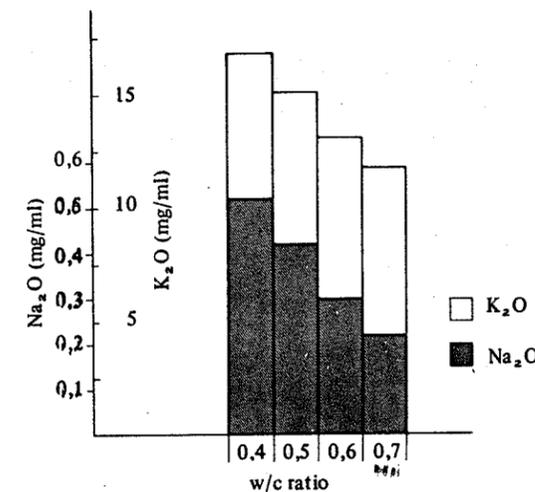


FIGURE 3: Alkali concentration in the pore solution at the time of the first contact with the aggregate.

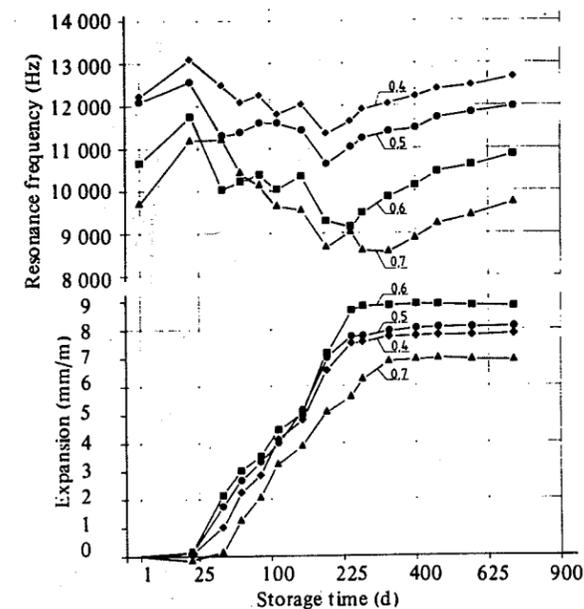


FIGURE 4: Expansion and natural resonance frequency of mortar specimens prepared with various w/c ratios.

Within the range investigated, the concentrations were found to be inversely proportional to the w/c ratio.

The mortar specimens were demolded after one day of wet curing. They were then stored in a slightly evacuated desiccator above water.

3. RESULTS

The progress of the ASR was followed by measuring the expansion and the natural resonance frequency of the mortar specimens.

For the data given in Figure 4 each curve represents the mean value of three equal specimens.

The damage caused by the ASR is indicated by a simultaneous expansion and decrease in natural resonance frequency. In the specimens with the w/c ratios 0,4, 0,5 and 0,6, it starts after about 25 days. The expansion and the decrease of the natural resonance frequency of the specimens with w/c = 0,7 starts only after 40 days.

The difference in the starting values of the natural resonance frequency clearly reflects the influence of the w/c ratio on the mortar strength.

The termination of expansion damage is indicated by an increase in the natural resonance frequency. This points to a strength gain due to the cementation of fractures.

In specimens with lower w/c ratios (0,4 and 0,5) termination was reached after about 190 days. In the specimens where w/c = 0,6, an increase in the natural resonance frequency was measured after 230 days and in those of w/c = 0,7 only after 330 days.

The largest expansion was measured in the specimens where the w/c ratio = 0,6. As they also underwent the most pronounced decrease in the natural resonance frequency, it can be said that the pessimum w/c ratio is 0,6. This statement, however, is only valid for the materials and mix proportions used in these tests.

In investigations with a mortar with a higher cement content and with 10 per cent siliceous magnesian limestone, Jones and Tarleton³ found the pessimum w/c ratio to be 0,4.

Furthermore, the pessimum w/c ratio should largely depend on the grain size of the reactive aggregate as the reaction rate of the ASR depends on it⁴.

As the permeability decreases with increasing hydration and curing time, it can be assumed that the pessimum w/c ratio will be higher when the reactive aggregate is coarser.

The test results clearly indicate that the rate of the deleterious reaction decreases with increasing w/c ratio.

4. EFFECT OF PLASTICISERS

In order to improve the concrete quality and/or its workability, more and more plasticizers are being used. These admixtures are adsorbed at the surface of the cement particles. They cause a better dispersion of the particles and facilitate their dislocation by reducing the surface tension of the water and/or by a lubrication effect.

Through the application of a plasticiser, either the w/c ratio can be reduced and so the concrete strength can be increased, maintaining the same workability, or at constant w/c ratio, the workability can be improved.

DISCUSSION

Prof S Diamond (Purdue University, USA) noted that the increase in resonance frequency after expansion had stopped, seemed to indicate that a crack healing process was taking place, and asked Dr Lenzner whether he had examined the specimens in an attempt to determine the nature of the process involved.

Dr D Lenzner said he thought it was well known that the reaction between alkali silicate and lime led to a solidification of the material. He had found that concrete cores which had at first exuded reaction products had later solidified as a result of carbonisation. Both processes caused the cementation of the cracks which had been produced by the reaction.

Dr P E Grattan-Bellew (NRC, Ottawa, Canada) observed that with the reactive hornfels in South Africa healing did not seem to have taken place, certainly on the structures examined while on the excursion, most of the cracks seemed to be quite open.

Dr D Lenzner said this was correct, because they had not been completely filled with reaction product. However, at the places where the cracks were filled, the reaction product had been solid and hard. Some healing could be found even when the crack was only partly cemented, it need not be completely filled.

Mr C Semmelink (NITRR, Pretoria) said that from his observations of some structures in the South Western Cape it appeared that the reaction product was often leached out of the cracks. There was one particular structure, built in 1948, which displayed the typical cracking pattern but there was no sign of any reaction product in the cracks.

Dr D Lenzner said that a normal observer could only look at the surface and did not really know what had happened in

the interior. He thought the reaction product would not be leached out from the interior.

Mr D St John (DSIR, New Zealand) reported that he had looked at quite a number of concretes in thin section and said he agreed with Mr Semmelink that it was very unusual to find the cracks filled in a concrete which had suffered from alkali-aggregate reaction. In concretes where the so-called autogenous healing was supposed to have taken place the only things he had ever been able to find in cracks were calcium hydroxide and calcium carbonate.

Dr D Lenzner agreed but added that nobody could tell exactly how deep the cracks reached into a structure. The wide-open cracks that were visible were probably only in the surface layer. They had taken cores from the interior of an affected structure and in the first hour had seen no cracks. The fact that cracks had developed only after 24 hours indicated that the concrete had been under stress.

Dr G Idorn (Denmark) said that many of the cracks that could be seen on the surface of a structure were simply the result of tensile stresses caused by expansion in the interior. They were a consequence of the reaction but might not themselves be involved at all.

Dr U Ludwig (RWTH, Aachen, West Germany) thought that the healing depended on both the width of the crack and on the overall humidity. From his research on the influence of humidity it was known that healing was much less when overall humidities were low and that a certain level of humidity was necessary before any healing of small cracks took place at all.

Dr D Lenzner added that healing was not simply a solidification of the reaction product but included the further hydration of as yet unreacted cement clinker.

S252/26

expansion accompanied by a steep decrease in the natural resonance frequency, an early rehealing is indicated by an increase in frequency. After 180 days, the reference specimens which meanwhile have expanded to be the same degree seem to be more severely damaged as indicated by their lower natural resonance frequencies.

For a more general determination of the influence of plasticisers on the ASR, further investigations are necessary, especially with higher w/c ratios.

ACKNOWLEDGEMENT

The investigations described in this paper are part of a research project which is financially supported by the Deutsche Forschungsgemeinschaft.

REFERENCES

1. KROGBEUMKER G *Beitrag zur Beurteilung des Zementsteingefüges in Abhängigkeit von der Mahlfeinheit, dem Wasserzementwert und der Hydratationstemperatur.* Diss TH Aachen, 1971.
2. POWERS T C COPELAND L E HAYES J C and MANN H M *Permeability of Portland cement paste.* Journ ACI 1954/55.
3. JONES F E and TARLETON R D *Reactions between aggregates and cement, Part VI.* H M Stationery Office, London, 1958.
4. LENZNER D and LUDWIG U *Alkali aggregate reaction with opaline sandstone.* Proc 7th Intern Congr Chem Cem Paris, 1980.
5. LENZNER D and LUDWIG U *Alkali reaction with opaline sandstone from Schleswig-Holstein.* Proc Fourth Intern Conf Effects of Alkalis in Cem and Concr West Lafayette, USA, 1978.
6. HOBBS D W *Influence of mix proportions and cement alkali content upon expansion due to the alkali-silica reaction.* Cem Concr Ass Techn Rep No 534, 1980.
7. LAWRENCE C D *Changes in composition of the aqueous phase during hydration of cement pastes and suspensions.* Highway Research Board Special Rep 90, 1966.
8. VERBECK G J and GRAMLICH C *Osmotic studies and hypothesis concerning alkali-aggregate reaction.* Proc Amer Soc Test Mat 55, 1955.
9. JAMBOR J *Influence of water-cement ratio on the structure and strength of hardened cement pastes.* Proc Hydraulic cement pastes: Their structure and properties, Sheffield, 1976.
10. DEPKF F M *Wirkungsweise und Anwendung von Betonverflüssigern.* Betonwerk + Fertigteil-Technik 3 1975.