THE EFFECT OF ADMIXTURES ON ALKALI-AGGREGATE REACTION IN CONCRETE

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Abstract

With expansion measurements on concrete containing opal as alkali-reactive aggregate the efficiency of admixtures was tested. Several fly ashes, trass, ground cristobalite and a SiO_2-glass dust were used as admixtures. The specific surfacec of the substances ranged from 2800 to 24000 cm^2/g.

The tests showed that the efficiency of admixtures can only be judged if not part of the cement, but a part of the fine sized aggregate in the concrete is replaced. For this judgement the specific surface is important too. Alkali expansion in concrete can be prevented completely by suitable dust-fine admixtures. The efficiency of admixtures is due to the chemical reactivity with alkalis in the pore solution and possibly also to an increased pore volume in the concrete. Glasses with medium SiO_2-contents seem to be more suitable than glasses or crystalline substances with SiO_2 contents of more than 95 % by weight. The use of admixtures is limited by requirements for the concrete quality, such as strength, watertightness and freeze/thaw resistance.

1. Introduction

Former investigations have shown that the course and the extent of the alkali-aggregate reactions in concrete are dependent on the alkali reactivity, the quantity and the grain size distribution of the aggregate, the alkali content of the cement, the cement content and the environmental conditions[1,2,3]. The knowledge from these extensive tests served as a basis for working out a recommendation with special attention to the conditions in North Germany. In this recommendation precautionary measures against a deleterious alkali-aggregate reaction have been laid down[4].

The precautionary measures are primarily based on an examination of the alkali reactivity of the used aggregate. Practical experience has shown that it is only the content of opaline sandstone and of reactive flint which is decisive and which is therefore determined with established testing procedures[5]. As a further precautionary measure the use of cements with low effective alkali content (NA-cement) has been introduced. These cements are required only for cases in which the aggregate has a certain amount of reactive constituents and the concrete additionally is exposed to disadvantageous environmental conditions. Such environmental conditions are for instance the permanent wetting of a construction and an alkali supply from outside, for instance by seawater or de-icing salts.

Further precautionary measures, which have not been incorporated in the recommendations, are the reduction in the cement content, if possible, according to the quality of the concrete. In some cases a better aggregate grading can also be of benefit. Also the addition of a more or less large amount of natural or artificial pozzolans to the concrete is often regarded as an effective measure to avoid a deleterious alkali-aggregate reaction. In order to examine the effectivity of such pozzolans it is necessary to distinguish whether a part of the cement or a part of the aggregate shall be replaced.

Admixtures which are thought to prevent deleterious alkali expansion are for instance fine-ground silica, opaline rock, volcanic glasses, diatomeen earth, trass, calcined clay and also fly ashes[6,7]. It is assumed that this effect is chiefly due to the chemial reactivity of the silica in such admixtures with the alkali hydroxide in the pore solution. If that is true, a shift of the pessimum of the reactive aggregates originally present should occur. Experiments with opal as a reactive admixture showed that it is in particular the opal quantity substituted in the quartz grain sizes < 0.2 mm that can prevent alkali expansion[8,9], if the sum of the opal quantity originally present and the opal quantity added is larger than the pessimum concentration of the reactive aggregate. It seems that besides opaline rocks no other admixtures have been tested in this way.

The majority of the experiments to test the effect of admixtures followed ASTM C 441. In that case not the aggregate, but a portion of 5 to 40 % by weight of the cement is replaced. Very often the water-cement ratio too had to be increased in order to maintain the workability of the concrete. With such a test procedure the found reduction in the expansion of specimens might be either the result of a pozzolanic reaction of the admixtures or the result of a dilution of the cement quantity. According to former investigations[3] such a reduction of the cement content is associated with a decrease in the effective alkali or OH^--content in concrete. This alone would therefore already lead to a drastic reduction in the alkali expansion.

From test results so far known it can be assumed that the various substances recommended as admixtures apparently show different chemical reactivity. Decisive might be in which form the reactive proportion of the silica is present and which grain size or surface the admixture has[6,7]. Occasionally it is also recommended to improve the effect of natural or artificial pozzolans by finer grinding[10] or by remelting with the addition of lime[11].

The effect of various admixtures could be examined more reliable, if they were tested under the same conditions. This means that the cement content and thus the effective alkali content in the concrete have to be kept unchanged. For these tests a part of the aggregate and not a part of the cement should therefore be replaced by the admixtures.

In addition to the chemical reactivity of the admixture the physical properties of the hardened cement paste, of the aggregate and of the concrete may also influence alkali expansion. It has already been stated that a deleterious alkali-aggregate reaction not only requires a high reactivity of the aggregate constituents, but also a low porosity [1]. This in particular applies to opal and various glasses which in normal case have no marked porosity. Experiments on flints with densities of < 2.53 to > 2.59 g/cm^3, on the other hand, showed with an approximately equal reactivity alkali expansion decreases as soon as the porosity rises. Similar to the effect of the porosity of the aggregate could be that of the capillary porosity of the hardened cement paste, leading with increasing water-cement ratios of the concrete to a reduction in the expansion. For this reason some additional tests have been performed to learn more about the influence of the capillary porosity.

2. Tests

In accordance with ASTM C 441 concrete specimen 2.5 x 2.5 x 28.5 cm were produced. The concretes contained approximately 600 kg cement per m^3 with a constant water-cement ratio of 0.45 [1]. It was only in a further test series that larger amounts of water were added to the concretes to increase the capillary pore volume in the hardened cement paste. The water-cement ratios were thereby increased to 0.60. The aggregate consisted of 6 fractions with a maximum grain size of 15 to 16 mm. As a reactive aggregate constituent pure opal in the grain size < 0.09 mm was chosen and added to the concrete in a quantity of 4 % by weight, based on the aggregate. This quantity was equal to the pessimum concentration for opal in that fraction. The specimens are stored at 40 °C and more than 95 % relative humidity. The results obtained so far are related to a storage time of 2 months.

Up to 20 % by weight of the aggregates were replaced by the admixtures trass, fly ash, cristobalite and an amorphous-glassy silica product (SiO_2-glass dust) mainly in the size fraction < 0.2 mm. The concretes containing admixtures were tested with and without opal.

	DENSITY [G/CM^3]	SPECIFIC SURFACE [CM^2/G]
QUARTZ	2,65	-
OPAL	2,06	-
CRISTOBALITE	2,35	3 500
SIO_2-GLASS	2,21	24 000
TRASS	2,42 - 2,48	5 800 - 6 300
FLY ASH	2,20 - 2,44	2 800 - 3 300

Fig. 1: Density and specific surface of used additives and aggregates

The table presented in fig. 1 shows that the trass had a specific surface according to Blaine of approximately 6000 cm^2/g. The surface of the fly ashes and of the cristobalite dust ranged from 2800 to 3200 cm^2/g. With approximately 24000 cm^2/g the SiO_2-glass dust showed the greatest fineness. The measured densities of the admixtures were in the range of 2.20 to 2.48 g/cm^3.

3. Test results

3.1 Porosity of the hardened cement paste

The experiments were carried out on concretes with an unchanged cement content of approximately 600 kg per m^3 and with 4 % by weight of opal, based on the aggregate. The fresh concrete mixes contained different quantities of water with a water-cement ratio ranging from 0.40 to 0.60.

The capillary porosity of the hardened cement paste in relation to the water-cement ratio was calculated by a method described by F.W. Locher[12]. For this purpose a hydration degree of the cement of 1 was presumed. Taking into account the chemical shrinkage, capillary pores are formed in a concrete with a water-cement ratio of more than 0.36, which increase the total porosity of the concrete. In fig. 2 the expansion of the concrete specimen was plotted versus the calculated volume of the capillary pores of the hardened paste.

It shows that with water-cement ratios exceeding 0.48 and a capillary porosity of 15 % by volume respectively the expansion due to alkali expansion falls linearly. The decrease is approximately 1 mm/m per 0.03 water-cement units. With lower water-cement ratio respectively pore volume the influence diminishes due to perhaps still uncomplete hydration of the cement and an uncomplete compaction of the concrete specimen.

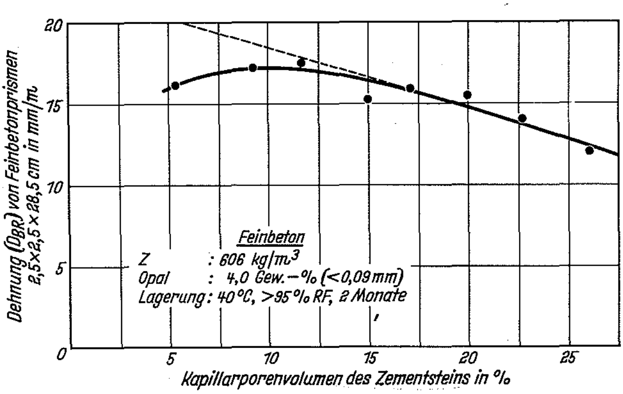

Fig. 2: Influence of the capillary pore volume of the hardened cement paste on the expansion of opal containing concrete specimen.

Further experiments have still to be carried out to investigate the physical properties of the prisms. But already now it can be concluded that the porosity of the hardened cement paste and of the concrete might help to reduce measurably the expansion caused by alkali aggregate reaction. The reaction product formed seems to be able to penetrate partly into the open pore spaces of the concrete and of the hardened cement paste. Therefore a comparison of the chemical efficiency of admixtures or a test of other influencing factors is only possible if besides the concrete composition the water-cement ratio also remains unchanged.

As a precaution against alkali expansion an increase in the capillary porosity is not suitable, since it reduces the concrete strenght and furthermore lowers the diffusion resistance to the ions penetrating from outside[13].

3.2 Chemical reactivity of admixtures

The expansion of a concrete which contained besides quartz sand and gravel 4 % by weight of opal was taken as basis for calculating the percentage of length change in all the other concretes. After 2 months the measured expansion of that reference concrete averaged 17.5 mm/m. The expansion of all other concretes which contained graduated amounts of admixtures besides 4 % by weight of opal are presented in fig. 3.

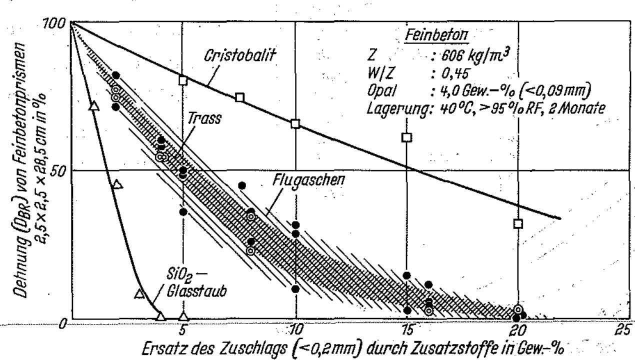

Fig. 3: Decrease of expansion by several kinds of admixtures independent on their specific surface area (Blaine). The quantity of admixtures is based on the total amount of aggregate.

It can be seen that all admixtures which were used instead of quartz sand diminish the expansion of opal-containing concrete. In concretes which with respect to workability contained 20 % by weight of cristobalite at the most, expansion was only reduced to approximately 30 %. It seems that in this kind of presentation the SiO_2-glass dust was the most effective admixture, because an addition of 4 to 5 % by weight at the most was sufficient to prevent the expansion entirely. A medium position with a reduction of expansion to a range of 60 to 35 % was taken by fly ashes (wide hatching) and trass (narrow hatching).

However, this presentation does not give any information about the grade of reactivity of the various admixtures since there is no uniform comparative basis. Owing to their different surface areas the substances were added in different quantities to the concrete. This was necessary in order to achieve a consistency which still allowed complete compaction of the concrete. To study the influence of quantity and surface of the admixtures together, the specific surface of the admixtures was multiplied with the quantity of the substance in 1 m^3 concrete.

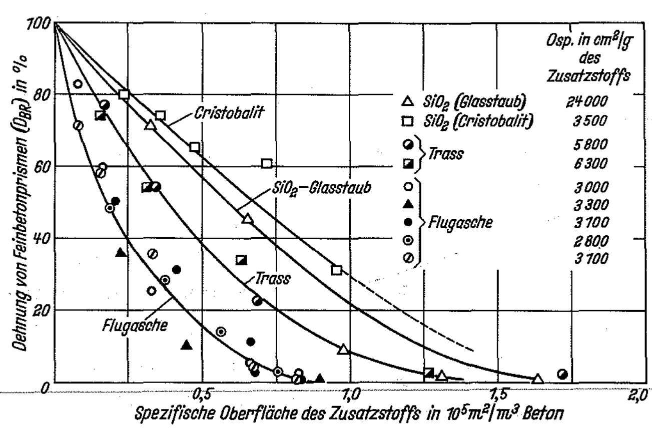

Fig. 4: Decrease of expansion by several kinds of admixtures according to their specific surface area (Blaine) and quantity in concrete.

In fig. 4 the percentage expansion of the concrete prisms has been plotted versus the total specific surface of the admixture per m^3 concrete. This again shows that the expansion decreases with rising surface proportions of the admixture. But on the basis of an equally large surface proportion of for instance $0.5 \cdot 10^5$ m^2 per m^3 of concrete it is found that fly ash glasses seem to be more reactive than trass, than cristobalite and the almost pure SiO_2-glass dust. On the basis of that evaluation also the differences between the 5 fly ashes became smaller. This is apparently due to the fact that the ashes of pit-coals from the Ruhr-Carbon have roughly the same composition and that they have been formed under similar conditions. The influence of their different alkali content is still to be tested.

The test results allow the conclusion that all admixtures react chemically with the pore solution in the concrete thus binding alkalies. At equal surface areas their efficiency is manifested in a more or less pronounced reduction of the concrete expansion caused by opal. But the admixtures tested are evidently more inactive than opal. Depending on their surface, admixture contents of up to 15 % by weight, based on the quantity of the aggregate, are necessary to reduce the expansion to values under 20 %. Using opal as an admixture this would only require an addition of a further 4 % by weight.

The alkalies bound by the admixtures apparently do not lead to a measurable expansion. This was proved by experiments on concrete specimen which contained the same graduated amounts of admixtures instead of quartz < 0.2 mm, but no opal. Although the used admixtures react with alkalies, they seem to have no measurable pessimum in this grain size. However, according to Australian[14] investigations expansions can be measured as soon as the grain size of some of these admixtures exceed 0.2 mm.

The effect of fine ground admixtures with such a relatively small reactivity seems to be based on the formation of alkali silicates which have an alltogether higher molar SiO_2-content than the silicates formed by reaction between alkalies and opal in pessimum concentration. First experiments have already shown that SiO_2-rich alkali silicates swell considerably less with water than alkali-rich silicates. That means, that according to the chemical reactivity of the used admixtures the pessimum of the reactive opal aggregate will be shifted.

Besides the chemical effect of admixtures also a change in the physical properties of the concrete has to be taken into consideration. Many of the used admixtures contain a pore space of 1 (Trass) to nearly 20 % of volume (fly ash), which increases the pore space of the concrete and may possibly work as a reservoir for reaction products thus reducing an expansion.

4. Conclusions

The investigations lead to the conclusion that the efficiency of admixtures can only be judged under constant test conditions. For that reason not a part of the cement, but only a part of the aggregate in the size fraction < 0.2 mm should be replaced. The concrete composition should remain unchanged. Besides this the mass-related specific surface of the admixture should be taken into consideration.

The investigations have shown that the expansion of opal-containing aggregates in the concrete can be avoided by the use of suitable admixtures. Their efficiency is mainly due to the chemical reactivity, but possibly also to an increase in the total pore volume of the concrete. The pore volume may be increased as well by admixtures as in the case of higher water-cement ratios also by the capillary pores in the hardened cement paste.

The reactivity of glasses with SiO_2-contents of approximately 50 % by weight is apparently greater than that of the tested crystalline substances with a similarly high SiO_2 content or that of the glasses and crystalline substances with more than 95 % of SiO_2, if the real quantity of active surface area is taken into consideration. To reduce alkali expansion it is therefore necessary to overtake fineness and quantity of the admixture into the requirements of a concrete mix. However, requirements for the concrete qualtity, such as strenght, watertightness and freeze/thaw resistance, limit the use of admixtures. An increase in the water-cement ratio in order to raise the capillary porosity or to improve workability is therefore no advisable measure.

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