



**ABOUT THE CAUSE OF THE RESISTANCE OF BLASTFURNACE CEMENT CONCRETE
TO THE ALKALI-SILICA REACTION**

by Dr R F M Bakker*

SYNOPSIS

In practice concretes made with blastfurnace cement containing more than 65 per cent slag, display an increased sulphate resistance compared with concretes made with ordinary Portland cement. They are also more resistant to the alkali-aggregate reaction. The reasons for this are not fully understood.

Experiments demonstrate that a reason for the resistance of blastfurnace cement concrete is not that the slags bind, but rather that they release, alkalis which are present in the slag in solid solution.

Experiments demonstrate that the behaviour of blastfurnace cement concrete, with respect to the alkali-aggregate reaction, can be explained by their very low permeability for ions and water. This explains why the alkalis in blastfurnace cements, with high slag content, are of no importance, as expressed in the German directives and at the same time explains the high sulphate resistance of blastfurnace cements with high slag content.

SAMEVATTING

In die praktyk toon beton van hoogoodsement wat meer as 65 persent slak bevat 'n verhoogde sulfaatweerstand vergeleke met beton van gewone Portlandsement. Dit is ook meer bestand teen die alkali-aggregaatreaksie. Die rede hiervoor is nog nie heeltemal duidelik nie.

Eksperimentele resultate toon dat die verklaring vir die weerstand van hoogoodsementbeton is dat alkalië uit die slakke vrygestel word eerder as dat die slakke alkalië bind.

Daar word met eksperimente gedemonstreer dat die gedrag van hoogoodsementbeton, wat die alkali-aggregaatreaksie betref, weens die besonder lae deurdringbaarheid vir ione en water verklaar kan word. Dit verklaar waarom alkalië in hoogoodsement met hoë slakinhoud onbelangrik is soos in die Duitse riglyne aangetoon en verklaar terselfdertyd die hoë sulfaatweerstand van hoogoodsement met hoë slakinhoud.

S252/29

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

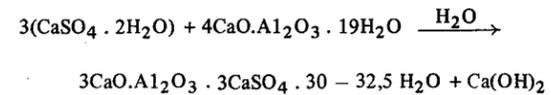
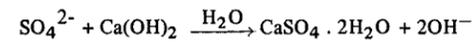
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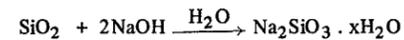
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1. INTRODUCTION

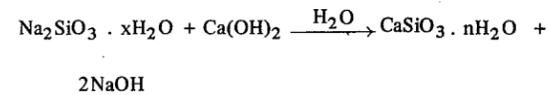
Concretes made with blastfurnace cement with high slag content (≥ 65 per cent slag) show an increased sulphate resistance compared to concretes made with ordinary Portland cement^{1, 2, 3}. Research done at the "Forschungsinstitut der Zementindustrie V D Z" has shown that the risk of detrimental alkali-silica reactions in concrete is small when using these blastfurnace cements with high slag content⁴. The reactions, which in both cases lead to detrimental expansions, are totally different. In the case of a sulphate attack, the reaction sequence is⁵:



In the case of an alkali-silica reaction the reaction is⁶:



The injurious alkali-silicate can be converted to the harmless calcium silicate



This different behaviour of blastfurnace cement with high slag content must be caused by an essential difference between the two cement types. The usual explanation of this behaviour with respect to *sulphate attack* is the low lime content of blastfurnace cement^{7, 8, 9}. Another explanation is the low tricalciumaluminate content⁷. In both cases the explanation is founded on the difference in *amount* of one of the reacting components, compared with ordinary Portland cement. The usual explanation of the behaviour of blastfurnace cement with respect to the *alkali-silica reaction* is the binding of the alkalis by the slag component¹⁰. Again the explanation is thought to be a difference in the *amount* of one of the reacting components.

All these explanations are based on the assumption, that in practice the theoretical equilibrium (minimum free enthalpy) will be reached in a reasonable time. The reaction velocity, however, in addition to the equilibrium plays a prominent part. The fact, that in diluted solution, on stirring, inorganic reactions do reach their equilibrium in a very short period of time, does not mean that in a complex concentrated non-stirred system, like cement stone, this is equally the case.

In the following it will first be shown that the binding of alkalis by the slag does not explain the different behaviour of blastfurnace cement in the alkali-silica reaction.

Next it will be shown that the difference in behaviour between Portland cement concrete and blastfurnace cement concrete can be explained by means of differences in the rate of diffusion of ions through them and in their permeability to water.

2. THE BINDING OF ALKALIS IN PORTLAND AND BLASTFURNACE CEMENT STONE

In general blastfurnace cements do contain more alkalis than Portland cements. On that account, blastfurnace cements with high slag content should present a faster or a greater expansion than Portland cements. The amount of alkali in the pore solution, however, is of primary importance. This amount does not necessarily correlate with the total amount of alkali in the cement.

The following experiment examines the extent to which the expansion of mortar is determined by the amount of alkali present in the pore fluid. The changes in concentration of the alkalis in the pore fluid were determined in the same manner as described by Locher, Richartz and Sprung¹¹. An ordinary Portland cement (OPC), a blastfurnace cement (BFC) and the same blastfurnace cement with high alkali content (BFC⁺, obtained by adding an amount of soluble alkalis) were compared. The composition of the cement paste is given in Table 1.

TABLE 1: Mix proportions of the cement paste

CEMENT TYPE	COMPOSITION OF THE SUSPENSION
OPC	25 g Portland cement (0,77 %Na ₂ O eqv) 50 g Distilled water
BFC	25 g Blastfurnace cement (0,89 %Na ₂ O eqv) (75 %slag) 50 g Distilled water
BFC ⁺	24,62 g Blastfurnace cement (0,89 %Na ₂ O eqv) 0,776 g Na ₂ SO ₄ · 10 H ₂ O (0,6 %Na ₂ O eqv) 49,6 g Distilled water

At the same time the expansion of these cements was measured according to ASTM C441 with the exception of the dimensions of the prisms and the W/C ratio. The experiments were carried out with prisms 40 x 40 x 160 mm and a constant W/C ratio of 0,45. The composition of the mixes is given in Table 2.

The results of the measurement of the changes in alkali content in the pore fluid and the expansion of the prisms are shown in Figures 1 and 2 respectively.

TABLE 3: Diffusion coefficients of Na and K ions in mortars made with Portland and blastfurnace cement after different hardening times

Hardening time of mortar (days)	Diffused ion	D_m in 10^{-8} cm ² /s	
		OPC	BFC
3	Na ⁺	7,02	1,44
	K ⁺	11,38	2,10
14	Na ⁺	2,38	0,10
	K ⁺	3,58	0,21

From the results it follows that the rate of diffusion of alkali ions through a three-day-old mortar of Portland cement is about five times faster, and through a two-week-old mortar about fifteen times faster, than through the equivalent blastfurnace cement mortar. A further divergence of the rate of diffusion can be concluded from the fifty to one hundred fold difference in the rate of diffusion of chloride ions through about three-month-old mortars of the same composition¹⁴. From these differences in rate of diffusion it follows that a potential detrimental reaction in blastfurnace cement mortar will proceed 50 - 100 fold slower than in Portland cement mortar.

4. THE PERMEABILITY TO WATER

For the expansion of concrete to take place as a result of the alkali-silica reaction it is necessary to have not only enough alkali but also a sufficient quantity of water. The water has to be transported to the place where the alkali-silicate has been formed. The permeability of the mortar to water consequently plays an important role in the rate at which expansion sets in. Alkali silicate locked up in concrete can build up pressure in the concrete by attracting water from its surroundings. As is shown by McConnell, Mielenz, Holland and Greene this pressure may crack the concrete¹⁵.

In blastfurnace cement mortar the alkali silicate will be formed more slowly than in Portland cement concrete as a result of the low rate of diffusion of alkali ions. In order to eliminate this difference and to concentrate solely on the difference in permeability to water, the following experiments were carried out. Hollow mortar cylinders were filled with alkali silicate (water-glass) and after providing the cylinders with a rubber stopper with a capillary tube, they were placed in a water bath, Figure 4.

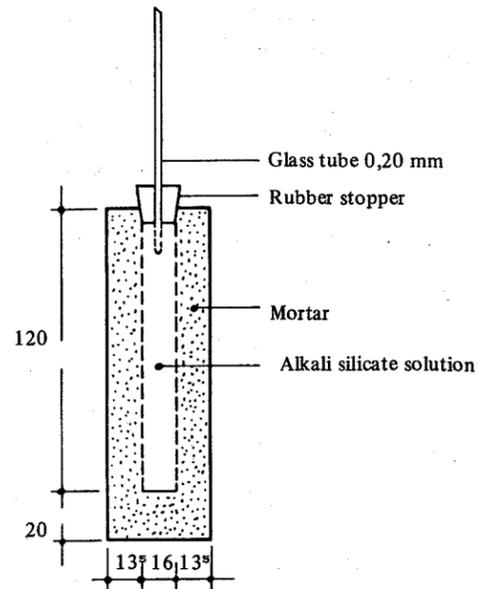


FIGURE 4: Mortar cylinder with glass tube and rubber stopper

The flow of water through the mortar was determined by measuring the rising liquid level in the capillary tube. The composition of the mortars is shown in Table 4.

The results of the flow measurements after different hardening times and at different water bath temperatures are shown in Figures 5 - 10, page 4.

TABLE 4: Mix proportions of the mortars and the water-glass

Mortar No	Cement type	A/C ratio	W/C ratio
1	OPC	2,0	0,50
2	BFC	2,0	0,50
3	OPC	2,8	0,65
4	OPC	2,8	0,65

- BFC slag content: 75 per cent (m/m)
- Aggregate: sand < 1 mm
- Water glass: 10,6 % (m/m) KOH and 23,8 % (m/m) SiO₂

TABLE 2: Mix proportions of the cement mortar

CEMENT TYPE	COMPOSITION OF THE MORTAR
OPC	472 g Portland cement (0,77% Na ₂ O eqv) 211 g Water (W/C : 0,45) 1062 g Pyrex*
BFC	472 g Blastfurnace cement (0,89% Na ₂ O eqv) 211 g Water (W/C : 0,45) 1062 g Pyrex*
BFC ⁺	465 g Blastfurnace cement (0,89% Na ₂ O eqv) 204 g Water (W/C : 0,45) 15 g Na ₂ SO ₄ · 10 H ₂ O 1062 g Pyrex*

* Grading in conformity with ASTM C441

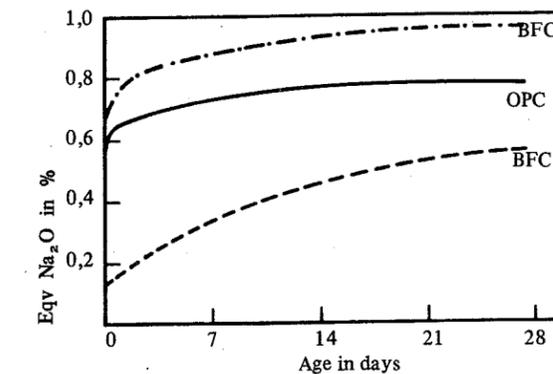


FIGURE 1: Release of alkalis during hydration (W/C = 2)

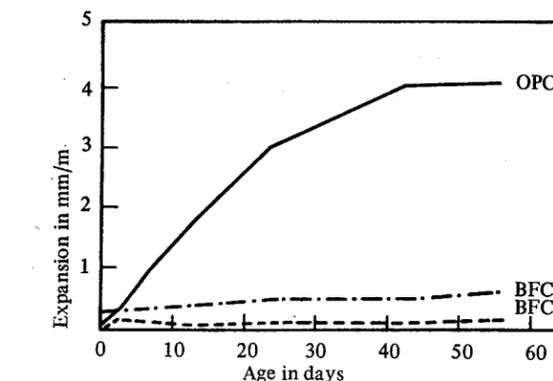


FIGURE 2: Expansion of mortar bars for three different cements determined by ASTM C441

From these figures it follows that there is no relationship between the amount of alkali in the pore solution and the expansion of the mortar made with alkali reactive aggregates. At the same time it follows from Figure 1 that the alkalis in blastfurnace cement with advancing hydration go into solution as is the case with Portland cement. It can be concluded that the difference between Portland and blastfurnace cement is not determined by the difference in the amount of alkali set free, but by other properties. The same conclusions were drawn by Cox, Coleman and White¹².

3. THE RATE OF DIFFUSION OF IONS

The rate at which the detrimental alkali-silicate is formed, depends on the rate at which the alkalis diffuse to the reactive silica. The rate of diffusion of several ions in Portland cement stone has been determined by Kondo, Satake and Ushiyama¹³. The diffusion coefficients of sodium and potassium hydroxide in Portland and blastfurnace cement mortar (W/C ratio 0,50; A/C ratio 2,0) were determined by a method similar to that described by these authors. Sand < 1 mm was used as aggregate. A cross section of the diffusion cell is shown in Figure 3.

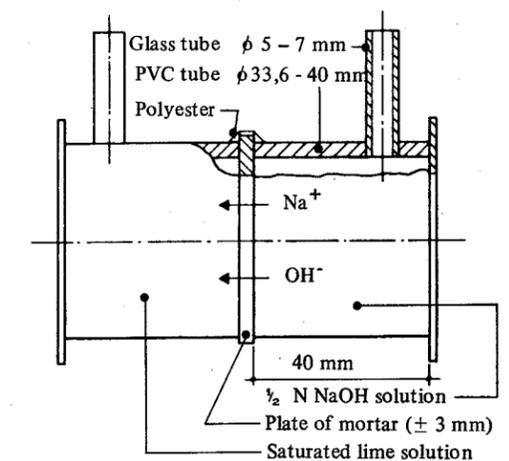


FIGURE 3: Cross section of the diffusion cell

The diffusion coefficients after different hardening periods are shown in Table 3.

From the results it appears that blastfurnace cement mortar is ten to one hundred fold less permeable to water than Portland cement mortar. The transport of water through a blastfurnace cement mortar comes practically to a standstill after a certain hardening time. From these experiments it follows that in blastfurnace cement mortar not only the difference in rate of diffusion of alkalis, but also the permeability to water is responsible for the behaviour of this cement with respect to the alkali-silica reaction. An eventual detrimental reaction will therefore proceed a hundred to a thousand fold slower in blastfurnace cement concrete than in Portland cement concrete.

5. ANALOGY WITH SULPHATE ATTACK

In the introduction it was stated that concrete made with blastfurnace cement with high slag content is proof against sulphate attack. The favourable behaviour of blastfurnace cement in this regard can be explained in the same manner as its behaviour in the alkali-silica reaction. For the development of expansion caused by the presence of sulphate ions, the transport of ions and water is necessary. The diffusion of sulphate ions and the transport of water is retarded in such a way that the detrimental reactions do not or hardly take place. These conclusions are supported by the findings of Locher, that blastfurnace cements can form ettringite with sulphates¹⁰. For this formation, however, intensive mixing of the cement stone with the sulphates is necessary. By this mechanical process the physical barriers are continuously broken down, so that the reaction can proceed. In hardened mortar, however, there is no mixing and hence no mechanical destruction of the barriers. Thus ettringite is for all practical purposes not formed as has been shown experimentally.

6. CONCLUSIONS

The behaviour of blastfurnace cement with high slag content, in regard to both the alkali-silica reaction and sulphate attack, can be explained as being due to the same cause, namely the low permeability of blastfurnace cement stone to ions and water. It is therefore not by pure accident that blastfurnace cement with about 65-70 per cent slag content will withstand two totally different detrimental reactions.

At the same time it can be understood why the alkali ions in blastfurnace cement with a high slag content are of no importance with respect to the alkali-silica reaction, as is formulated in the German recommendations. (See table 5.)

TABLE 5: Requirements for cements with low alkali activity (NA cements)

	Alkali content in % (m/m) Na ₂ O eqv	Slag content in % (m/m)
Portland cement	≤ 0,60	---
Blastfurnace cement	≤ 0,90	≥ 50
	(≤ 2,00)	≥ 65

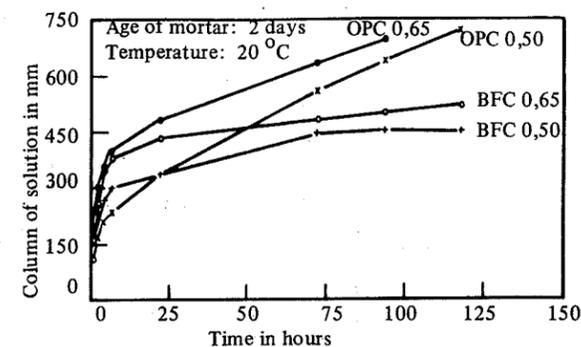


FIGURE 5: Change of the level of the solution as a result of diffusion through two-day-old mortars of different composition; water bath temperature 20°C

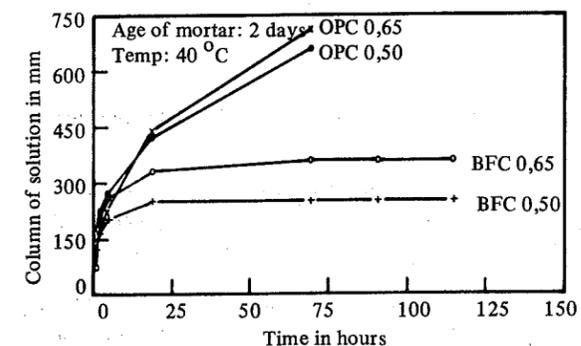


FIGURE 6: Change of the level of the solution as a result of diffusion through two-day-old mortars of different composition; water bath temperature 40°C

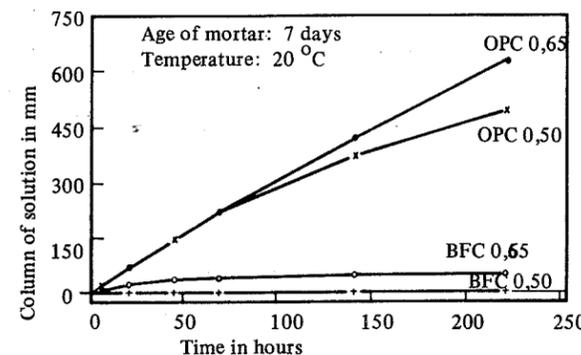


FIGURE 7: Change of the level of the solution as a result of diffusion through seven-day-old mortars of different composition; water bath temperature 20°C

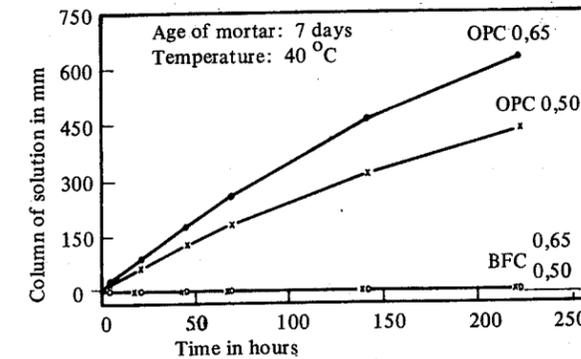


FIGURE 8: Change of the level of the solution as a result of diffusion through seven-day-old mortars of different composition; water bath temperature 40°C

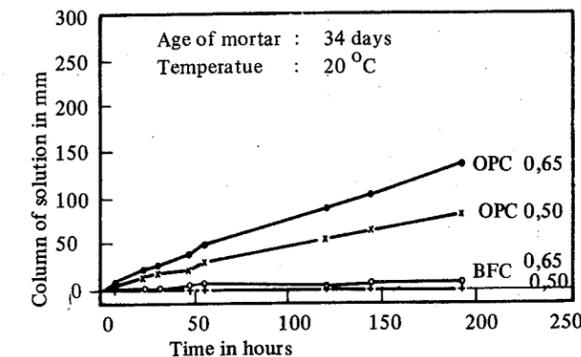


FIGURE 9: Change of the level of the solution as a result of diffusion through 34-day-old mortars of different composition; water bath temperature 20°C

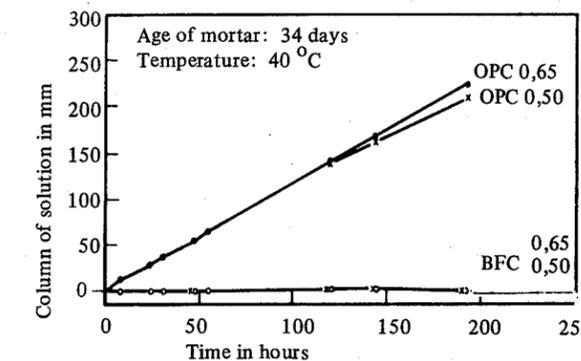


FIGURE 10: Change of the level of the solution as a result of diffusion through 34-day-old mortars of different composition; water bath temperature 40°C

DISCUSSION

Dr P E Grattan-Bellew (NRC, Ottawa, Canada) asked whether the pore size distribution of ordinary Portland cement mortar and blastfurnace cement mortar had been measured.

Dr Bakker said this had not been done because in most cases one would have to dry the specimen, with the result that the paste would crack and this in turn would affect the pore size distribution.

Mr G F Loedolff (University of Stellenbosch) asked why blastfurnace cement concrete was more dense than ordinary Portland cement concrete.

Dr Bakker replied that when ordinary Portland cement clinker hydrated, calcium hydroxide went into solution and a lot of calcium hydroxide crystals were formed. The space between the hydrating opc clinker particles was not filled by hydration products. When blastfurnace cement particles hydrated more aluminium and silica were set free and combined with calcium hydroxide from the opc clinker grains, to form more CSH gel and the space between hydrating grains was thus more properly filled.

Dr M Regourd (CERILH, Paris, France) added that with blastfurnace slag cement the CSH was markedly more compact, it was lower in calcium than opc CSH, and the pore size distribution was more compact.

Note: The last line of column 2 of Table 4 on page 3 of the printed paper should read BFC.

S252/29

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