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THE ALKALI-AGGREGATE REACTION: A CONTRIBUTION CONCERNING THE DETERMINATION OF THE REACTIVITY OF PORTLAND CEMENTS

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SYNOPSIS

An investigation to determine the reactivity in respect of the alkali-aggregate reaction between cements and Pyrex glass, Beltane opal and Malmesbury hornfels is described. It has been established that neither Pyrex glass nor Beltane opal can be used as reactive aggregates to determine the reactivity of cements. Hornfels could possibly serve as an aggregate to determine the reactivity of cements. The results show that there is a direct relationship between the expansion of mortar prisms made with hornfels aggregate and available alkalis from the cement. Thus some standardisation of the reactivity of cements, based on available alkalis, is possible in order to determine the alkali-reactivity of aggregates such as those from the Malmesbury Group.

SAMEVATTING

Die resultate van 'n ondersoek om die reaktiwiteit van semente met betrekking tot alkali-aggregaatreaksie met behulp van Pyrexglas, Beltane-opaal en Malmesbury horingfels te bepaal, word gerapporteer. Daar is gevind dat nóg Pyrexglas, nóg Beltane-opaal sondermeer as reaktiewe aggregate gebruik kan word om die reaktiwiteit van semente te bepaal. Horingfels hou moontlikhede in as aggregaat om die reaktiwiteit van semente te bepaal. Die resultate dui daarop dat 'n direkte verband tussen uitsetting van mortelprismas wat met horingfels as aggregaat gemaak is en beskikbare alkalie van die sement bestaan en dat daar 'n mate van standardisering van die reaktiwiteit van sement, gebaseer op beskikbare alkalie, vir die bepaling van die alkali-reaktiwiteit van byvoorbeeld Malmesbury aggregate gevolglik moontlik is.

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1. INTRODUCTION

If the reactivity of cements were known and could be standardised it would be possible to evaluate the potential alkali-reactivity of those aggregates that did not show a pessimum effect, and to compare the results obtained by different laboratories. It would promote a saving in both energy and materials if, by means of an efficient test, some cements which are today regarded as unsuitable for use with a reactive aggregate because of their total alkali content, could be found suitable.

Sprung[1], Bakker[2] and ASTM C441-69[3] refer to the use of Pyrex glass in their tests while Brotschi and Mehta[4] have done similar work with both Pyrex glass and opal as reactive aggregates. Besides these materials the authors have included a Malmesbury hornfels from the South Western Cape Province as a reactive aggregate in their investigations. The Malmesbury hornfels displays no pessimum effect and this gives rise to the possibility of using it to determine the reactivity of cements.

In this investigation seven South African Portland cements were tested to determine their reactivity. The aim was to determine accurately the alkali-reactivity of aggregates such as Malmesbury hornfels by means of the ASTM C227-71[5] prism test.

2. MATERIALS USED IN THE INVESTIGATION INTO THE REACTIVITY OF CEMENTS

Crushed Pyrex glass number 7740 or Duran 50 was used in the investigation as well as Beltane opal derived from the deposit in Sonoma County, California[6]. Hornfels from the Malmesbury Group (NBRI[7]) was also used. The petrographic examination showed that the hornfels was very fine-grained with an average grain size of 10 μm and contained approximately 45 per cent quartz, 25 per cent feldspar, 25 per cent matrix material and less than 5 per cent opaque minerals. By means of X-ray diffraction techniques it was established that illite/sericite, K-vermiculite and kaolinite were also present. The physical properties of the hornfels comply with the applicable requirements of standard specification SABS 1083-1976[8].

Five ordinary portland cements (total Na_2O-equivalent given in brackets; see Table 1) viz. A(0,16), B(0,82), C(0,62), D(0,85), F(1,02), one sulphate resisting cement G(0,58) and one cement F(1,30) were examined. The cement F(1,30) was obtained by adding sodium and potassium sulphate to cement F(1,02). Mortar prism tests with hornfels showed that the addition of small amounts of sulphate as gypsum ($CaSO_4.2H_2O$) had no perceptible effect on the expansion and consequently that no sulphate expansion can be expected from the small amounts of Na_2SO_4 and K_2SO_4 that were added. The cements complied with the applicable requirements of standard specification SABS 471-1971[9] and of SABS 626-1971[10] for autoclave expansion.

The sodium and potassium oxide contents of the cements are shown in Table 1. The figures for total alkalis and water-soluble alkalis (those that have dissolved in water after ten minutes of extraction at room temperature) were determined according to ASTM C114[11]. The ASTM C311[12] test method was employed for determining the available alkalis, with the exception that no lime was added to the cement. ('Available alkalis' implies those alkalis that have dissolved while the cement and water have been standing in a sealed container at 38 °C for 28 days).

(a) Pyrex glass

The expansion of Pyrex glass mortar prisms as a result of the reactivity of cement is used in the ASTM C441-69 test to indicate the suitability of admixtures for prevent-

TABLE 1 : Sodium and potassium oxide content of cements

	Cement						
	A(0,16)	B(0,82)	C(0,62)	D(0,85)	F(1,02)	G(0,58)	F(1,30)*
Total alkali, %							
Na_2O	0,04	0,33	0,48	0,25	0,24	0,26	0,33
K_2O	0,18	0,75	0,21	0,91	1,18	0,49	1,50
Na_2O equivalent**	0,16	0,82	0,62	0,85	1,02	0,58	1,30
Water soluble alkali, %							
Na_2O	0,01	0,12	0,08	0,02	0,09	0,05	0,16
K_2O	0,05	0,45	0,06	0,11	0,86	0,26	1,18
Na_2O equivalent	0,04	0,42	0,12	0,09	0,66	0,23	0,94
Available alkali, %							
Na_2O	0,04	0,28	0,39	0,19	0,21	0,17	0,28
K_2O	0,10	0,53	0,13	0,58	0,93	0,36	1,25
Na_2O equivalent	0,11	0,63	0,48	0,57	0,82	0,41	1,10

* Calculated from the analysis of F

** % Na_2O equivalent = % Na_2O + (% K_2O x 0,658) ing the alkali-aggregate reaction. A number of experiments have also been described in the literature[1,2,4] for determining the reactivity of cements by means of Pyrex glass, which for this purpose is regarded as a standard aggregate.

Mortar prisms made with Pyrex glass aggregate, and treated according to ASTM C441-69 requirements, showed very poor repeatability in the expansions obtained. For example, after 14 days the results varied between 0,037 and 0,165 per cent for cement F(1,30); between 0,09 and 0,14 per cent for cement F(1,02), and between 0,076 and 0,105 per cent for cement C(0,62).

Since it was suspected that the compaction of the glass mortar prisms influenced their expansion, prisms were prepared by compacting the mortar in several ways at different flow values. The total pore space of the prisms was obtained by determining the relative density according to ASTM C128-73[13] and the bulk density according to Venter and Oberholster[14]. The air voids were determined according to ASTM C457-71[15].

The preparation parameters, the total pore space and air void space obtained, can be summarised as follows:

F (1,30)(105V)(16,0)(1,4);
F (1,30)(105V)(19,1)(4,8);
F (1,30)(115)(20,6)(4,2);
F (1,30)(105)(21,3)(5,5);
F (1,30)(105)(22,8) (9,6) and
F (1,30)(115)(23,2)(10,7).

The first figure in brackets refers to the Na_2O equivalent of the cement, the second figure to the flow percentage (V shows that the prisms were compacted by vibration), the third figure indicates the total pore space, while the fourth gives the estimated air void space as a percentage of the total volume of mortar. The prisms compacted by vibration display the lowest porosity.

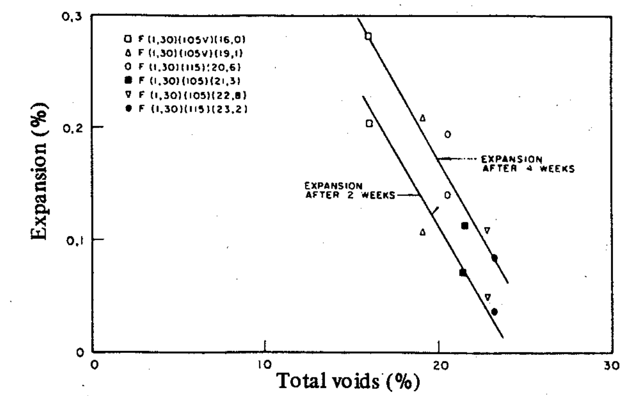

FIGURE 1: Influence of total pore space on the linear expansion of Pyrex glass mortar prisms. The prisms were stored according to ASTM C441-69 at 38 °C

The relationship between the pore space and the expansion of the glass mortar prisms after 2 and 4 weeks, respectively, is shown in Figure 1. The results agree with the findings of Vivian[16] that a reduction in the pore space (air void volume) is accompanied by an increase in expansion. The data show that the expansion is influenced by the method of compaction and also that there is a variation in expansion obtained for a specific method of preparation.

The influence of compaction on porosity and the resultant influence on the expansion of Pyrex glass mortar prisms can be reduced to some extent by making prisms with mixtures of glass and natural non-reactive sand. For example, a mixture made with 40 per cent Pyrex glass and 60 per cent sand with a good grain shape, will require less water to achieve the same flow as for mortar made with crushed glass only and will allow better compaction because of the better grain shape.

The expansion of mortar prisms in which 40 per cent Pyrex glass and 60 per cent natural sand was used, is shown

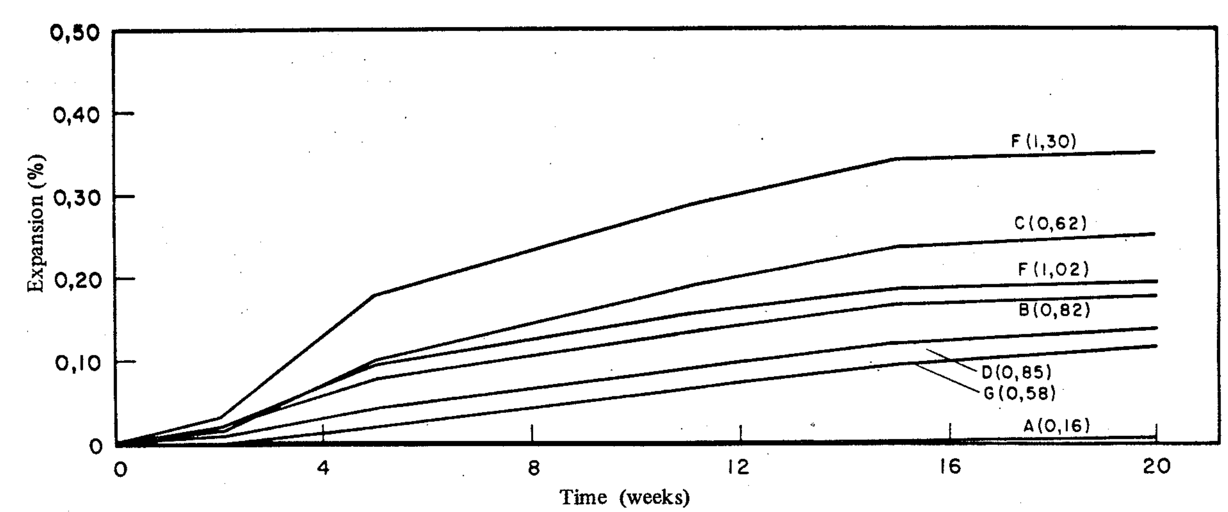

FIGURE 2 : Linear expansion of mortar prisms made with different cements and 40 per cent Pyrex glass and 60 per cent natural sand. Treated according to ASTM C441-69

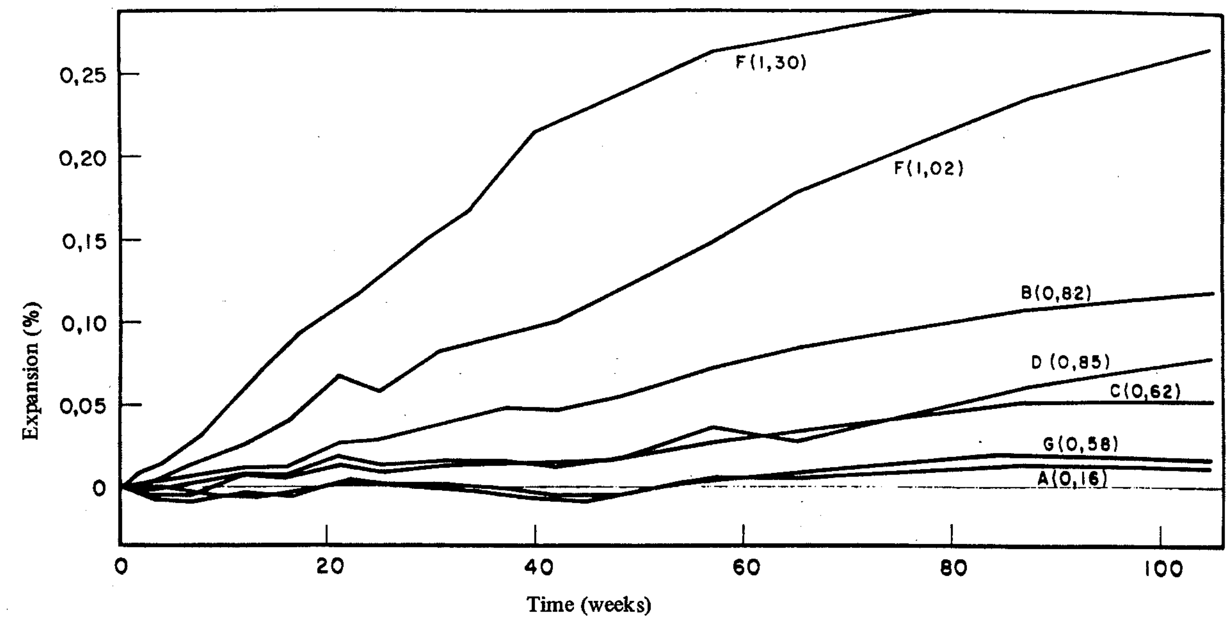

FIGURE 3 : Linear expansion of mortar prisms made with hornfels aggregate and seven different cements. The prisms were made and treated according to ASTM C227-71[5]

in Figure 2 for the seven cements with different alkali contents.

The expansion for the cement C(0,62) which, according to ASTM C150[17], can be regarded as a low alkali cement, is relatively high, whereas the expansion for the cement D(0,85), a high alkali cement according to ASTM 150[17], is relatively low. It can be concluded from the data in Figure 2 that within the 20-week treatment period no direct or significant relationship was detected between the expansion of the glass mortar prisms and either the water-soluble or the total alkali content of the cement (see Table 1).

(b) Opal

Opal is a siliceous mineral which could, as mentioned in ASTM C227-71[5], result in deleterious alkali-silica expansion if present in sufficient quantities in combination with a cement with an Na_2O equivalent of more than 0,6 per cent.

Prisms made with Beltane opal and a non-reactive natural sand in which a portion of the -300 µm + 150 µm fraction of the sand was substituted by 1, 2, 4, 6, 8, or 10 per cent opal, calculated as a mass percentage of the total aggregate, show a very strong pessimum effect, with the result that the degree of reactivity of the different cements is influenced by the percentage of opal in the aggregate. Opal is consequently unsuitable for determining the reactivity of cements.

(c) Hornfels

Because the Malmesbury hornfels is a naturally occurring expansive aggregate which has caused damage in the South Western Cape it was chosen as the material to use in the determination of the reactivity of South African cements.

The linear expansion of mortar prisms made with hornfels aggregate and each of the seven cements is illustrated in Figure 3.

The mortar prisms with cement C(0,62) do not show the high expansion obtained with Pyrex glass as aggregate (Figure 2) whereas prisms with cement D(0,85) show a relatively low expansion similar to that obtained with Pyrex glass as aggregate.

It is noteworthy that prisms which expand exhibit a continuing expansion even over 104 weeks despite the fact that those with expansions greater than 0,1 per cent show a definite crack pattern that could be expected to affect the expansion.

The expansion pattern shown in Figure 3 reveals a certain relationship between the expansion and the alkali content of the cements. The investigation was therefore extended to determine which of the parameters, viz., total alkali content, water-soluble alkali content or available alkali content, correlated the best with expansion. McCoy and Eshenour[18] regard water-soluble alkalis as the active part of the total alkali content of the cement. The expansion of hornfels and other Malmesbury aggregates, however, begins only after about 6 to 10 weeks in contrast to prisms made with Pyrex glass or opal where the expansion is more or less complete after 14 days.

For this reason the relationship between expansion and available alkali content determined according to ASTM C311[12], was also examined.

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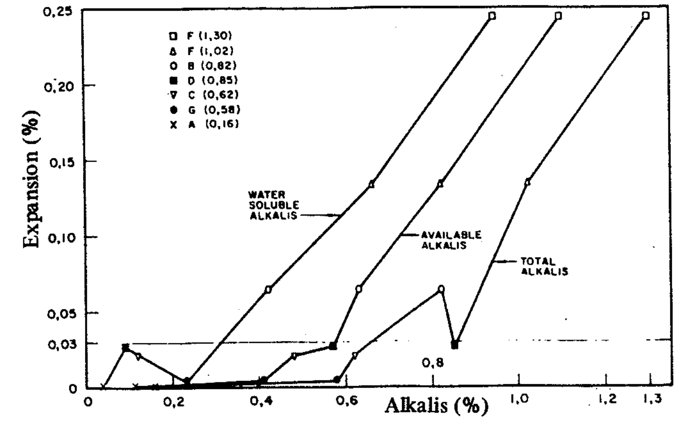

FIGURE 4: Relationship between linear expansion after 52 weeks and water-soluble, available and total alkalis. The prisms were prepared and treated according to ASTM C227-71[5]

The total, the available and the water-soluble alkalis are presented in Table 1. After 28 days between 63 and 85 per cent of the total alkalis are present as available alkalis. It appears at present that, beyond 28 days, the percentage of available alkalis does not increase significantly and that the available alkalis could, at this stage, be regarded as the active alkalis with regard to the alkali-aggregate reaction.

The relationship between the expansion after 52 weeks and the water soluble, available, and total alkalis, respectively, is illustrated in Figure 4.

The results in Figure 4 show that a significant relationship exists between expansion and the amount of available alkalis.

A good relationship also appears to exist between the expansion and the water soluble alkalis but, because the available alkalis are released over a long period of time and appear to be the principal agent of expansion, the relationship may be coincidental.

These results appear to show that the total alkali content of a cement is not a reliable measure for judging its reactivity. According to ASTM C150-78a[17] and ASTM C33[19] cement D(0,85) is a high alkali cement but it causes little expansion in combination with hornfels aggregate. Repetition of the tests showed a variation of approximately 15 per cent within the prescribed flow of ASTM C227-71[5] viz. 105 to 120 per cent. A higher expansion was obtained with a 105 per cent flow than with a 120 per cent flow. It was further established that variations in the air void content of the mortar prisms made with Tygerberg Formation rock as aggregate did not influence the expansion.

3. CONCLUSIONS

The results of the investigation into the reactivity of cements can, at this stage, be summarised as follows:

(a) Repetition of the Pyrex glass mortar prism test shows poor reproducibility of expansion. This can be attributed to factors such as compaction and flow (within the limits prescribed by ASTM C441-71), causing variations in porosity which in turn influence expansion.

The expansion of Pyrex glass mortar prisms does not appear to be related to either total alkali or water soluble alkali content.

The reason for the high expansion obtained with cement C(0,62) and Pyrex glass (Figure 2), which can be regarded as a low alkali cement, and the low expansion obtained with cement D(0,85), which is regarded as a high alkali cement, could also not be established.

(b) Beltane opal is unsuitable for determining the reactivity of cements since the expansion of prisms is strongly influenced by the pessimum effect.

(c) The determination of the available alkali content of a cement in order to establish its reactivity is promising because of the good relationship found between the available alkali and the expansion of mortar prisms containing Malmesbury hornfels aggregates (Figure 4).

The available alkalis constitute between 63 and 85 per cent of the total alkali content of the cements investigated. For example the available alkali of cement D(0,85) is 0,57 per cent (67 per cent of the total alkali content) which possibly explains why expansions obtained with this cement differ so little from expansion obtained with the low-alkali cement C(0,62).

The investigation further revealed that cement D(0,85) which according to ASTM C150[17], is a high alkali cement, has a low reactivity and is unsuitable for determining the alkali reactivity of some aggregates. Malmesbury hornfels falls into this group.

Further work in this regard needs to be carried out and 15 cements are at present being investigated.

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DISCUSSION

Dr D W Hobbs (C & CA, London) felt that the strange results obtained with the Beltane opal were as a result of specimens with a common Beltane opal content being tested and compared. A comparison was therefore being made in which different alkali reactive silica ratios had been used. If the comparisons had been made at approximately a common most critical alkali reactive silica ratio, a much clearer picture would have been obtained.

Dr F S Buttler (Teesside Polytechnic, England) referred to the alkalis of the cements which were quoted as Na_2O equivalent. He asked whether the sodium and potassium content for all of these cements was known and whether the potassium had been high in cement C (Figure 2). He stressed his concern with the fact that potassium was converted into sodium when referring to an Na_2O equivalent; the chemistry of Group I ions in aqueous solutions was very different, thus when studying possible reactions, the mobility within the pore fluid of potassium should have been greater than that of sodium because potassium's hydrated ion size was smaller.

Mr Brandt replied that all the high alkali cements, with the exception of cement C, had Na_2O contents of about 0,3 per cent and higher K_2O than Na_2O. For cement C the Na_2O was higher than the K_2O. However, he stressed that with the Pyrex glass method, ASTM C441-69, the expansion was measured at 14 days. Within this period of 14 days the active alkalis, which were determined in the experiments after 28 days, had not all been released. A cement which released most of its alkalis within the first 24 hours would give a completely different expansion rate (would expand differently) to a cement which released a relatively greater proportion over a longer period; with the Pyrex glass method one did not have complete control over these factors.

Prof S Diamond (Purdue University, USA) who was the only member of the ASTM committee responsible for the relevant test methods present, commented that the test methods were not entirely satisfactory. He had in fact reviewed them in an ASTM publication about 2 years ago, STP 169B. He then responded to some of the substansive points which had been raised with the following thoughts. One of the difficulties with the use of Pyrex glass as specified by ASTM was that until very recently the Pyrex glass specified was in the form of lump cullet. This was a waste product, consisting of waste glass which was partly remelted and despite the fact that Pyrex composition generally was very well controlled, one could not be sure what variations existed in the lumps. There was thus a built-in variability which caused all sorts of difficulties in tests. He felt, however, that a major source of difficulty was really one of philosophy. In his view, attempting to treat the cement and the aggregate as reactors, with the expansion being the indication of the product of reaction, was not an accurate assessment of the true situation. He felt that there was a reaction between dissolved alkali hydroxides in the pore solution and whatever reactive aggregate might be available. The product of this chemical reaction was gel of a variable composition which was not very well controlled, and could differ from place to place even within the same mortar bar. The secondary physical chemical reaction was expansion caused by the absorption of fluids by this gel. That could vary locally within the same mortar bar from place to place and would be reflected only in a very general way as an overall expansion in the mortar bar. The expansion was conditioned by small differences in humidity, by temperature gradients, by all sorts of potential differences between one sample and its neighbour. As a result there was no straightforward cement-aggregate expansion situation. There was a dissolved alkali-aggregate reaction and then possibly some further expansion which depended on a host of factors.

Mr Brandt explained that he had not used lump cullet but Pyrex laboratory glassware. He asked for Prof Diamond's opinion of the test for evaluating mineral admixtures.

Prof Diamond replied that he felt the test was defective.