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ALKALI REACTIVITY OF SILICEOUS ROCK AGGREGATES :  
DIAGNOSIS OF THE REACTION, TESTING OF CEMENT AND  
AGGREGATE AND PRESCRIPTION OF PREVENTIVE MEASURES

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1. ABSTRACT

In some badly cracked concrete structures containing orthoquartzite aggregate the cause of the deterioration is not immediately evident on site. Consequently concrete specimens have to be examined in an attempt to identify the reason for the deterioration.

Two possible methods for the determination of the active alkali content of cements are described.

Limits for the mortar and concrete prism methods performed under ASTM C227 conditions have been established for siliceous rock aggregates. An accelerated mortar prism test is described and limits proposed. Two variations of the quick chemical test to identify alkali-reactive aggregates, are discussed.

Limits for the active alkali content of concrete containing alkali-reactive siliceous aggregates have been established for a 0 per cent/100 per cent risk situation.

Keywords: reaction products, accelerated test methods.

2. INTRODUCTION

Although alkali-aggregate reaction was recognised in South Africa for the first time in 1974 a coordinated research effort into the problem was commenced only in the second half of 1977.

The aim of the research effort has been to obtain data with a view to advising laboratories on test methods, specification authorities on probable limits, consulting engineers and construction companies on precautionary measures, owners of structures on remedial measures and aggregate producers and cement manufacturers on the overall significance of the problem.

This paper is not intended as a review of the current status of research in South Africa but will present a brief account of some of the important or interesting developments since the last conference on this subject, held in 1981.

3. DIAGNOSIS

The visual appearance of concrete in the field that has been affected by alkali-aggregate expansion has previously been described /1/. However, situations arise where more definite evidence of alkali-aggregate reaction is required, for example where expansion is evident but sulphate attack is a possibility or where concrete is badly cracked but signs of expansion are not clearly observed. Under these circumstances examination of concrete taken from the structure and the characterisation of the reaction products in it are required.

The following data are for concrete from a number of structures in the Eastern

Cape that are badly cracked but where clear signs of expansion could not be observed. Since the only cement factory in this area manufactures a high-alkali cement and the orthoquartzite aggregate has been found to be potentially alkali reactive in laboratory tests, the concrete was examined for evidence of alkali-aggregate reaction.

### 3.1 Characterisation of reaction products in concrete

The typical occurrence of reaction product on the fracture surfaces of aggregates, in other words, occurring on planes where the aggregate ruptures along cracks or joints, was only observed in concrete from one structure (see Figure 1).

However, the optical properties of the reaction products in the concrete of all the structures correspond well with those from structures in the south western Cape, namely, a light brown, anisotropic mineral, with a salt and pepper appearance and refractive indices between 1,502 and 1,510 and a colourless anisotropic product with refractive indices between 1,494 and 1,502.

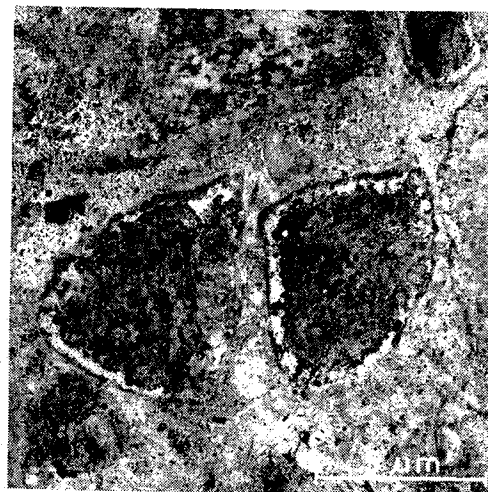
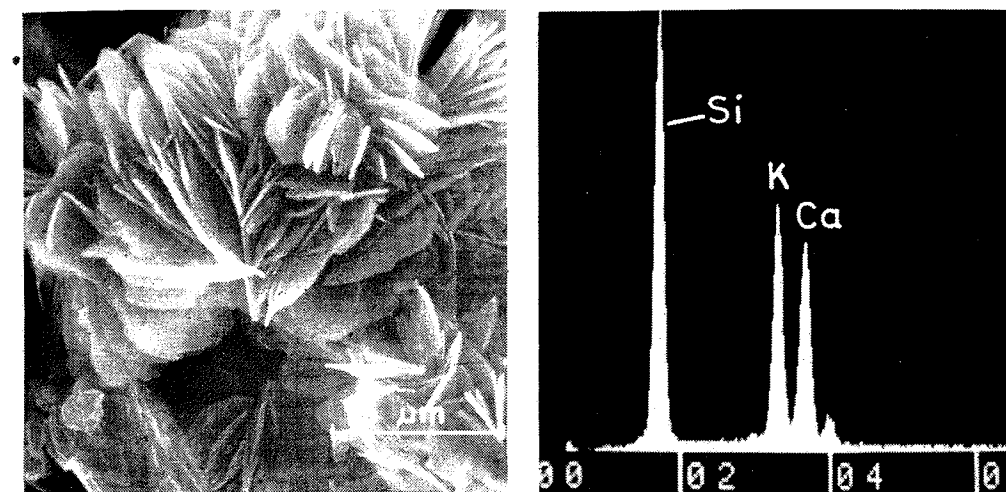


Figure 1. Typical deposit of reaction product observed when aggregate fractures along a weak plane such as a crack. Concrete from abutment of Gamtoos River bridge containing orthoquartzite aggregate.

The platy rosette-like crystals observed with a scanning electron microscope and shown in Figure 2(a) are typical of the reaction product found in structures affected by alkali-aggregate reaction in the south western Cape and are similar to reaction product reported by for example Regourd et al /2/ and Cole et al /3/. The EDXA and EMPA data shown in Figure 2(a) and Table 1 respectively are also similar to those reported by the above authors, although

in the average compositional formula of  $0,08CaO \cdot 0,04K_2O \cdot (0,01Al_2O_3 \cdot 0,99SiO_2)$  given by Cole et al the C/S and K/S ratios are appreciably lower.



(a)

(b)

Figure 2. (a) Scanning electron micrograph of reaction product in void, pier, Gamtoos River bridge.  
(b) EDXA pattern of reaction product.

The results of an X-ray diffraction analysis of the reaction product in concrete from five structures in the Eastern Cape, the Lansdowne bridge (LDB) in the south western Cape and a dam in Australia /3/, are given in Table 2.

It is seen that different structures apparently have sets of d-values in common. Some of the variation encountered between structures, might be ascribed to the fact that the reaction product is sensitive to changes in moisture content and very easily loses or gains water with an accompanying decrease or increase in d-values, as illustrated by the values for the Lansdowne bridge where the recording was done with a Guinier camera with and without vacuum being applied.

Only the crystalline components of the reaction product are identified by XRDA and not amorphous components. Apart from quartz which originates from the aggregate and hydration products of the cement, probably more than one crystalline product is present in the reaction product.

### 3.2 Expansion of concrete cores stored under ASTM C227 conditions

The reason for storing concrete cored from a structure under ASTM C227 /4/ conditions is that, if a reactive combination of cement and aggregate has been



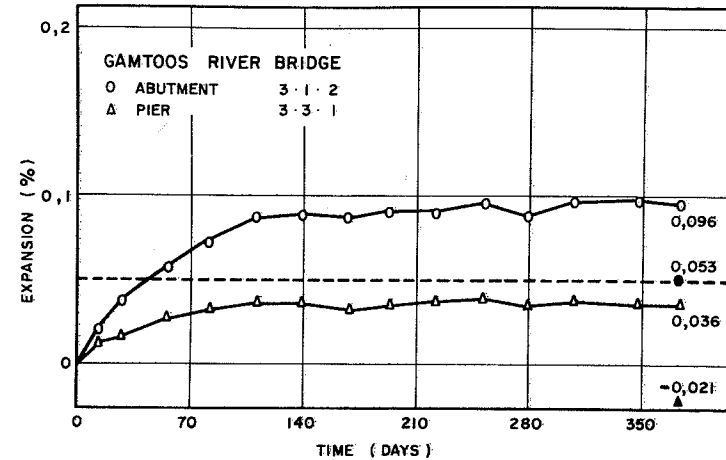


Figure 3. Linear expansion of concrete cored from a bridge and stored above water in a sealed container at 38°C. The solid symbols indicate the values obtained at termination of the test, after the concrete had been dried at 55°C and 17 per cent relative humidity to constant length.

in addition to wetting expansion will occur. In concrete where alkali-aggregate reaction has already taken place, additional reaction and expansion may be little or may not occur at all because either the alkali or the reactive constituent in the aggregate may have been exhausted by the initial reaction in the structure. Even if additional reaction may occur, expansion may not follow because the reaction product is insufficient to fill the cracks which are already present in the aggregate and the mortar.

Once cracking has occurred, expansion will not be completely reversible on drying.

For the concrete of which the results are presented in Figure 3 the drying shrinkage and wetting expansion were respectively 0,065 per cent and 0,058 per cent for the abutment and 0,043 and 0,026 for the pier.

From the results it is concluded that the concrete from the abutment expanded more under ASTM C227 conditions than can be ascribed to normal wetting expansion. The values for drying shrinkage and expansion on wetting are also excessive. In the case of the pier it is clear that the concrete was not dry at the commencement of the test and also that the total dimensional change is high. However, the results are inconclusive as to whether the movement is due to normal drying shrinkage/wetting expansion or to the alkali-aggregate reaction.

### 3.3 Summary

(i) The reaction products identified in concrete containing orthoquartzite aggregate are similar to those found in structures that have deteriorated as a result of alkali-aggregate reaction and in laboratory specimens.

(ii) The reaction product is a calcium-potassium-silicate with average C/S = 0,21, K/S = 0,08 and K+N/S = 0,11. The main diffraction peak occurs at about 12,2 Å. This peak can very easily shift to about 11,1 Å if care is not taken to avoid moderately high temperature or vacuum during the examination of specimens.

(iii) Circumstantial evidence points to alkali-aggregate reaction being a cause of deterioration of the structures containing orthoquartzite aggregate. However, it is not certain whether the products identified in the concrete specimens and which are associated with alkali-aggregate reaction, are the ones that caused the initial expansion.

(iv) It is not easy to determine whether the expansion obtained from concrete cored from structures and stored under ASTM C227 conditions can be ascribed to alkali-aggregate reaction. Care should be exercised in the interpretation of the results.

## 4. TESTING CEMENT AND AGGREGATE

### 4.1 Cement

The necessity of standardising cement in respect of its reactivity with an alkali-reactive aggregate (in other words its silica reactivity) was previously stressed by Oberholster et al /6/. Subsequently it was shown that the available alkali content of a cement determined according to ASTM C311 /7/, but without the addition of calcium hydroxide, was a good indicator of the reactivity of a cement. Consequently, the alkali content of a cement determined by this method is taken as its active alkali content /8/.

Although this method is excellent for the standardisation of cement to be used for the determination and comparison of the reactivity of aggregates or for the evaluation of cement-aggregate combinations it is not a suitable method for the day to day control of the active alkali content of a cement at the factory or for control purposes at a construction site, since it takes 28 days to obtain results.

Therefore, with a view to obtaining a quicker method, the 21 cements used in the original investigation were analysed for alkali content by the selective dissolution methods employed by Pollit & Brown /9/. Table 3 summarises the relationship between alkali content determined by various methods and the expansion of mortar prisms made with hornfels aggregate and the different cements and tested according to ASTM C227.

It is seen that the ASTM C311 method of determining the alkalis in cement gives the best measure of the active alkali content. A multiple regression analysis was therefore carried out to establish the relationship between the active alkali content as established by the above method and alkali in the various

TABLE 3. Correlation coefficients and regression equations for the relationship between expansion (Y) of mortar prisms and different forms of alkali (X), expressed as Na<sub>2</sub>O equivalent, of cement (n = 19)<sup>†</sup>

Alkalis	Correlation coefficient	Regression Equation
Total	0,8665	Y = -0,1614 + 0,2834X
Water soluble, ASTM	0,8196	Y = -0,0196 + 0,2229X
Active	0,9597	Y = -0,1312 + 0,2936X
Ethylene glycol, EG*	0,8462	Y = -0,0075 + 0,3123X
Water soluble, selective, H <sub>2</sub> O <sub>s</sub> *	0,6022	Y = -0,0563 + 0,6022X
EG + H <sub>2</sub> O <sub>s</sub>	0,8629	Y = -0,0485 + 0,2643X
Salicylic acid, HSA*	-0,2481	Y = 0,1360 - 0,2614X
EG + H <sub>2</sub> O <sub>s</sub> + HSA	0,9204	Y = -0,1397 + 0,3281X
Acetic acid, HAC*	0,0218	Y = 0,0866 + 0,0265X
EG + H <sub>2</sub> O <sub>s</sub> + HSA + HAC	0,9148	Y = -0,1755 + 0,3218X

<sup>†</sup>The two low-alkali, control cements were not included in the calculations.  
\*Alkalis determined in the filtrate during progressive selective extraction.

phases of cement. The best correlation was obtained with the following regression equation

$$\text{Active alkalis} = -0,0806 + 1,1241(\text{EG} + \text{H}_2\text{O}_s) + 0,8475\text{HSA} + 0,7664\text{HAC}$$

with a correlation coefficient of 0,9872.

Table 4 gives a comparison of the alkali content of 21 cements determined by different methods as well as the calculated values for active alkali content.

The possibility of using selective dissolution methods to determine the silica reactivity of cements in terms of their active alkali content is being investigated further, using the above regression equation.

#### 4.2 Aggregate

##### 4.2.1 Petrographic examination

Using the method of Dolar-Mantuani /10/ of determining the undulatory extinction angles of quartz, has proved to be successful in the provisional classification of rocks such as granite, granite-gneiss, orthoquartzite and arkose in respect of potential alkali reactivity. However, features such as suturing and polygonisation complicate matters when it is attempted to get an indication of the relative reactivity of aggregates by this method.

##### 4.2.2 Variations of ASTM C289

Brandt and Oberholster /8/ have reported a good relationship between expansion of mortar prisms made with hornfels or greywacke aggregate and the amount of silica dissolved after 3 or 7 days in the ASTM C289 /11/ chemical test. It is proposed that more than 1 per cent SiO<sub>2</sub> dissolved after 3 days or more than 2

TABLE 4. Alkali content of twenty one cements

Cement	Percentage Na <sub>2</sub> O equivalent for			
	Total	Water Soluble	Active	Active calculated
A(0,16)	0,16	0,04	0,11	0,11
B(0,82)	0,82	0,42	0,63	0,63
C(0,62)	0,62	0,12	0,48	0,47
D(0,85)	0,85	0,09	0,57	0,54
E(0,73)	0,73	0,43	0,62	0,68
F(1,02)	1,02	0,66	0,82	0,85
F(1,30)	1,30	0,94	1,10	1,17
G(0,58)	0,58	0,21	0,41	0,43
H(0,97)	0,97	0,60	0,82	0,83
J(0,82)	0,82	0,66	0,80	0,78
K(0,98)	0,98	0,35	0,79	0,80
L(1,12)	1,12	0,92	1,04	0,98
M(0,94)	0,94	0,64	0,82	0,79
N(0,59)	0,59	0,32	0,49	0,46
O(0,33)	0,33	0,09	0,27	0,27
P(0,56)	0,56	0,11	0,40	0,38
Q(0,88)	0,88	0,66	0,82	0,85
R(1,22)	1,22	0,75	1,18	1,14
S(0,75)	0,75	0,41	0,68	0,71
T(1,14)	1,14	0,72	1,09	1,03
U(0,96)	0,96	0,33	0,75	0,79

per cent after 7 days indicates potentially alkali-reactive aggregates.

Van Aardt and Visser /12/ proposed the treatment of 10g of -600µm +300µm aggregate in 25 ml 1N NaOH plus 1g of Ca(OH)<sub>2</sub> at 80°C for seven days. Poorly defined XRD peaks between 12Å and 16Å as shown in Figure 4 for the gel separated from the mixture, appear to be a sure sign of an aggregate that will expand excessively.

##### 4.2.3 Mortar and concrete prism tests performed under ASTM C227 conditions

After examining a great number of aggregates in combination with cements of widely different active alkali contents and correlating the results with concrete specimens of the same cement-aggregate combinations exposed to natural environmental conditions the following criteria were decided on /8/.

- When evaluating cement-aggregate combinations, an expansion of more than 0,05 per cent within one year in both the mortar prism and concrete prism tests indicates a potentially deleteriously expansive combination.
- When testing aggregates, an expansion of more than 0,05 per cent in one year in combination with a cement with an active alkali content of 1,1 per cent Na<sub>2</sub>O equivalent for both mortar and concrete prisms containing respectively 600kg and 350kg cement per m<sup>3</sup>, in other words respectively

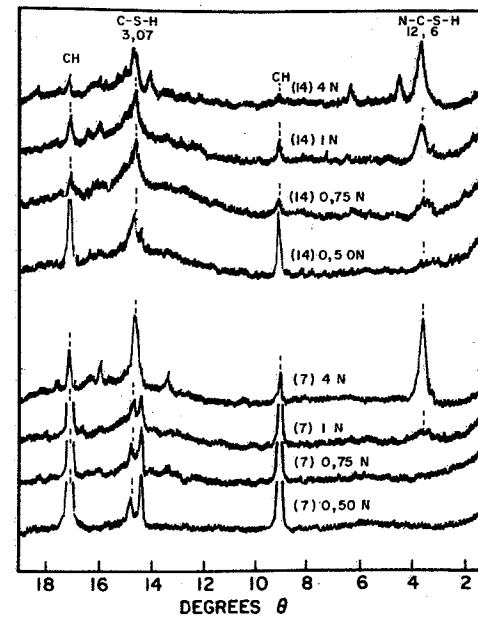


Figure 4. XRD traces for gel separated from reacted mixtures of hornfels aggregate plus CH in sodium hydroxide for 7 and 14 days /11/.

6,6kg and 3,8kg equivalent  $\text{Na}_2\text{O}$  per  $\text{m}^3$ , indicates alkali-reactive aggregates.

#### 4.2.4 Accelerated mortar prism test

Van Aardt and Visser /12/ have proposed a method whereby mortar prisms made with low alkali cement and the aggregate to be tested are stored in 1N NaOH at 80°C. Specimens are made in accordance with ASTM C227, demoulded after 24 hours, immersed in water and the temperature raised slowly to 80°C. The zero reading is taken 24 hours after the prisms have been conditioned at 80°C and then immersed in 1N NaOH at 80°C. Specimens are measured daily for 14 days at a room temperature of 23°C as soon as possible after removal from the container at 80°C without the temperature having dropped much. No indication was given by the authors of possible limits that indicate potentially alkali-reactive aggregates.

The method was therefore evaluated using a number of alkali-reactive and non-reactive siliceous aggregates that had previously been tested with the mortar and concrete prism tests as well as with Beltane opal replacing between 2 and 30 per cent (m/m), calculated as a percentage of the total aggregate, of the -300 $\mu\text{m}$  +150 $\mu\text{m}$  fraction of a non-reactive sand. The results are presented in Figures 5(a) and (b).

In Table 5 the results for concrete and mortar prisms made with a high-alkali cement with an active  $\text{Na}_2\text{O}$  equivalent of 1,28 per cent and stored under ASTM C227 conditions are compared with those of mortar prisms made with a low-alkali cement,  $\text{Na}_2\text{O}$  equivalent 0,24 per cent and subjected to the accelerated test.

Based on the available data, it is provisionally proposed that in the accelerated test an expansion of more than 0,08 but less than 0,20 per cent indicates slowly expansive siliceous rocks and 0,20 per cent and more, rapidly expansive siliceous rocks.

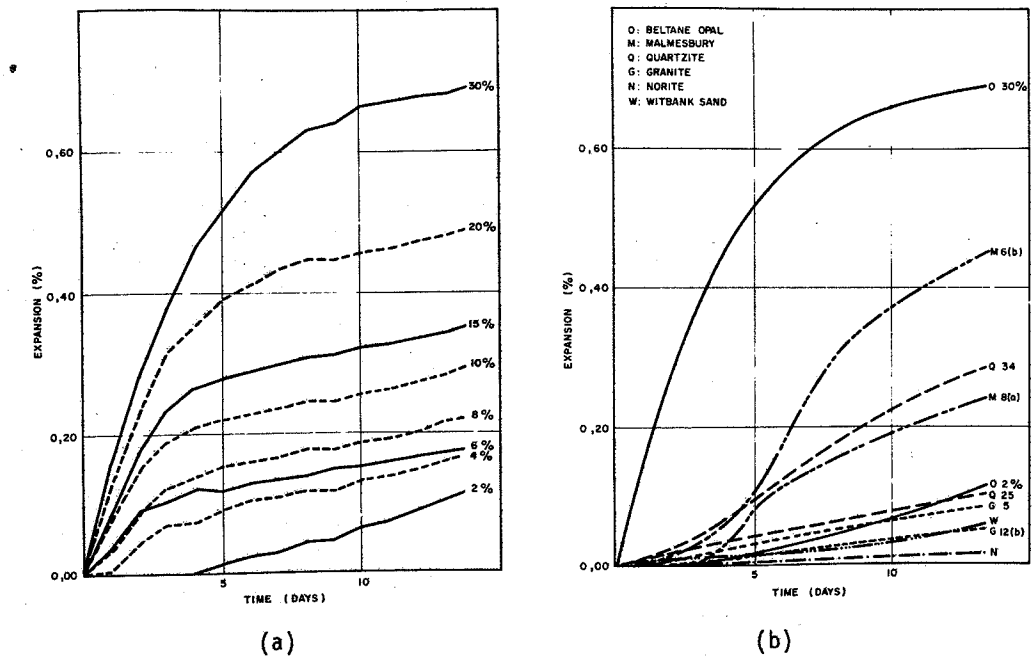


Figure 5. Linear expansion of (a) mortar prisms containing different percentages of Beltane opal aggregate and (b) mortar prisms made with a number of different aggregates. Stored in 1N NaOH at 80°C.

TABLE 5. Comparison of the expansion obtained with concrete and mortar prisms under ASTM C227 conditions after one year and mortar prisms in an accelerated test after 10 days

Test	Percentage linear expansion for					
	Hornfels/ greywacke		Quartzite		Granite	
	6(b)	8(a)	34	25	5	12(b)
Concrete prisms, ASTM C227	0,259	0,188	0,153	0,057	0,045	0,024
Mortar prisms, ASTM C227	0,120	0,075	0,215	0,096	0,016	0,027
Mortar prisms, accelerated	0,367	0,190	0,223	0,078	0,062	0,037



#### 4.3 Summary

(i) Cements can be standardised in respect of their active alkali content by employing the method for available alkalis (ASTM C311) or by selective dissolution methods.

(ii) Methods such as the determination of the undulatory extinction angle of quartz grains, silica dissolved in 1N NaOH at 80°C after 3 or 7 days and the XRDA of the gel formed when aggregate is reacted with CH and 1N NaOH at 80°C for 7 days, are suitable for the provisional identification of alkali-reactive aggregates.

(iii) The concrete and mortar prism tests performed under ASTM C227 conditions are suitable for the determination of the potential alkali reactivity of cement-aggregate combinations. Provided that the active alkali content of the cement used is specified these two tests are also suitable for the determination and comparison of the alkali reactivity of aggregates.

(iv) The accelerated test proposed by van Aardt and Visser /12/ is suitable for the determination of the alkali reactivity of aggregates.

#### 5. PREVENTIVE MEASURES

The potential of a concrete to expand due to alkali-aggregate reaction, will be a function of the active alkali content of the cement multiplied by the cement content, in other words the active alkali content of the concrete, and the reactivity of the aggregate. For an aggregate not showing a pessimum effect the rate of the reaction will therefore be a function of the product of the abovementioned two factors.

Figure 6 illustrates the above two points namely with each of the two cements F(1,30)(1,10)\* and B(0,82)(0,63) a range of expansions is obtained for concrete prisms made with different Malmesbury aggregates and the rate of expansion is higher for cement F(1,30)(1,10) than for B(0,82)(0,63). Even the least reactive aggregate expands more than 0,05 per cent in less than one year with cement F(1,30)(1,10). Therefore, concrete with an active alkali content of 3,8kg Na<sub>2</sub>O equivalent per m<sup>3</sup> (the cement content of the prisms was 350kg per m<sup>3</sup>) and containing Malmesbury aggregate is without doubt deleteriously expansive. However, only a certain percentage of aggregates expand more than 0,05 per cent in one year in combination with cement B(0,82)(0,63). This means that at an active alkali content of 2,2kg per m<sup>3</sup> Na<sub>2</sub>O equivalent concrete may be potentially deleteriously expansive depending on the reactivity of the aggregate. Likewise, it was established that in combination with cement C(0,62)(0,48) none of the aggregates gave an expansion of 0,05 per cent in one year. Therefore, concrete with an active alkali content of 1,7kg Na<sub>2</sub>O equivalent per m<sup>3</sup> and containing even the most reactive Malmesbury aggregate, is not potentially deleteriously expansive.

\*The first figure in brackets indicates the total alkali content and the second figure the active alkali content expressed as per cent Na<sub>2</sub>O equivalent.

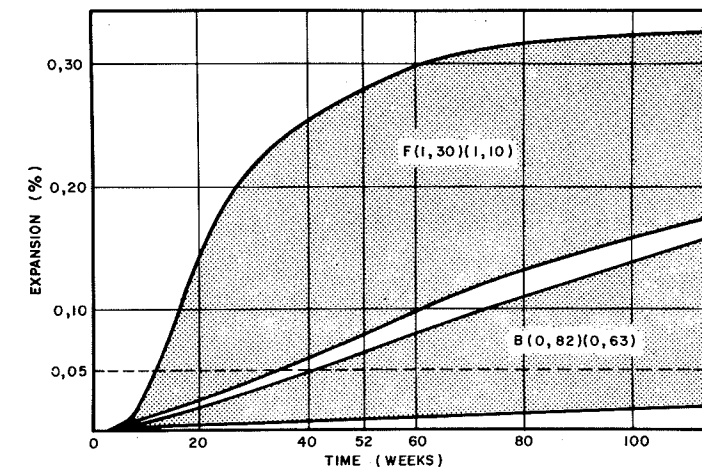


Figure 6. Range of linear expansions of concrete prisms made with different Malmesbury aggregates and cements F(1,30)(1,10) and B(0,82)(0,63). Prisms stored under ASTM C227 conditions /8/.

For exposed concrete made with Malmesbury aggregate the following is therefore concluded:

- (i) Above an active alkali content of 3,8kg Na<sub>2</sub>O equivalent per m<sup>3</sup> deleterious expansion will always occur.
- (ii) Between 3,8 and 1,8kg\* Na<sub>2</sub>O equivalent per m<sup>3</sup> the potential for expansion will depend on the reactivity of the aggregate and the active alkali content of the concrete.
- (iii) Below 1,8kg Na<sub>2</sub>O equivalent per m<sup>3</sup> deleterious expansion will not occur.

Figure 7 graphically illustrates the above limits.

These limits of course apply only to Malmesbury aggregate in the south western Cape. The graph should only be used to identify the upper limit where expansion will definitely take place and the lower limit where it will not, and not for assessing any "degree of expansion risk". For orthoquartzites of the Table Mountain Group for example, the upper limit where all the aggregates expand deleteriously after one year is 4,5kg active Na<sub>2</sub>O equivalent per m<sup>3</sup> and the lower limit where none expand deleteriously after one year, 2,8kg active Na<sub>2</sub>O equivalent per m<sup>3</sup>.

\*The 0,48 per cent Na<sub>2</sub>O equivalent is rounded off to 0,5 per cent.

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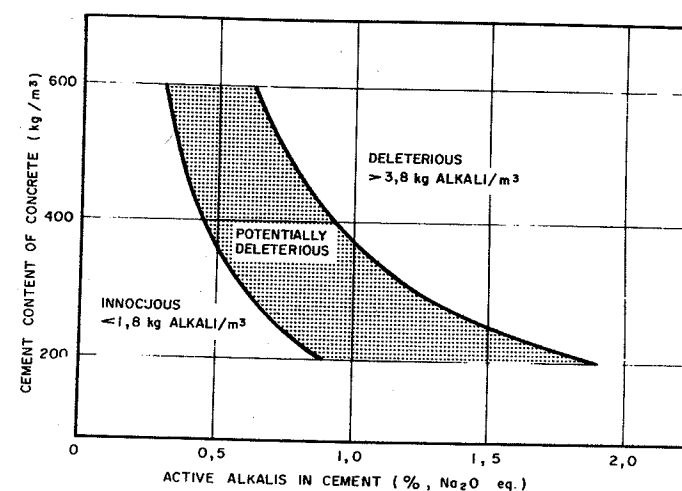


Figure 7. Relationship between the active alkali content of cement, the cement content of concrete and the resultant potential of the concrete for alkali-aggregate reaction.

It seems therefore, that with the possibility of determining the alkali reactivity of an aggregate quickly with the accelerated mortar prism method and also the active alkali content of cement by selective dissolution analysis, the aim should be to construct a diagram which gives the relationship between the alkali reactivity of the aggregate, the active alkali content of the cement and the potential of the concrete made with a particular combination at different rates of cement content to undergo alkali-aggregate reaction.

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