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1. ABSTRACT

The principal reactive mineral in the cases of alkali silica reaction in the UK is cryptocrystalline quartz in flint and chert. The established test methods for alkali reactivity are of only limited value for UK aggregates. BRE research on AAR and the work going on within BSI to develop a method are described.

KEY WORDS - AGGREGATES, ALKALI REACTIVITY, TESTS

2. INTRODUCTION

The growth of the awareness of alkali aggregate reaction in the United Kingdom has been described by Allen /1/, Palmer /2/ and Gutt and Nixon /3/. In outline no cases of AAR were identified in the British Isles until 1971 when it was discovered in the Val de la Mare Dam on the island of Jersey. In 1976 cases were identified in the South West of England and later elsewhere on the mainland, in particular, in the valley of the River Trent. The current position is that somewhere in the region of 50 cases have been identified, with most of them occurring either in South West England, South Wales or the Trent Valley though odd cases have been identified elsewhere such as the Lowlands of Scotland or the East Coast of England.

3. AGGREGATE TYPES AFFECTED

In the UK the aggregate types affected by AAR fall into two main categories. The first of these are sands consisting largely of quartz but with cherts or flints* in the coarser gradings. It is the cherts or flints which are attacked by the alkalis. Sands such as these, dredged off the South Coast of England or in the Bristol Channel have been identified in concrete affected by AAR in the South West of England and South Wales where they have usually been used with an inert coarse aggregate such as crushed limestone or granite. Sands from the Thames Valley are similar though tending to have higher proportions of flint.

The aggregates in the second category are the sands and gravels from the Trent Valley. These contain only small proportions of chert, the remainder being mainly quartzites and quartz. The cherts have certainly been found to be attacked by alkalis and there is some less clear evidence that quartzites may also be attacked. Cases of AAR have been found both when the sands and gravels have been used together and when the sand has been used with an inert coarse aggregate.

Other isolated cases of AAR in the UK have involved exposed glass aggregate /4/ or in two cases in the Lowlands of Scotland, greywacke and felsite in the aggregate which was excavated on the construction site.

* as used here flint is chert occurring in or derived from chalk deposits

3.1 Mineralogy of the reactive aggregates in deteriorated concrete

When the flints and cherts attacked by alkalis are examined by optical microscopy in thin sections of the concrete the only forms of silica which can be identified are cryptocrystalline quartz and occasionally chalcedony. X-ray powder diffraction of aggregate particles taken from attacked concrete similarly gives only patterns for quartz or obvious impurities such as calcite. There seems to be a broad correlation between iron staining of the chert and evidence of attack. None of the chemically reactive species of silica such as opal, cristobalite or tridymite have been identified however.

In the Trent Valley aggregates there is some evidence that quartzites have been attacked though this is not as clear cut as in the case of the cherts.

4. INVESTIGATIONS OF BRITISH AGGREGATES

An extensive investigation of the susceptibility of British aggregates to attack by alkalis was undertaken at the Building Research Station in the 1940's and 1950's by Jones and Tarleton /5/. They used a number of methods, principally petrographic examination, a gel pat test and early versions of what were to become the ASTM chemical method C289 and the ASTM mortar bar method C227. The outcome of this work was that, using the gel pat and chemical methods, they found evidence of slight reactivity in some siliceous aggregates, particularly flints, but they found no deleterious expansions in the mortar bar tests. Most of their mortar bar tests were carried out at 20°C and they did express some concern about the possibility of flint aggregates being reactive at higher temperatures. Overall however their conclusions were that there was little cause for serious concern about alkali aggregate reaction developing with British aggregates.

This opinion was the accepted one until the field evidence for reaction in concrete became evident in the late 1970's. The investigations currently being undertaken at the Building Research Establishment are described below.

In the initial stages attention was focussed on sea dredged fine aggregates since these were used in the first structures identified as suffering from AAR. Later as cases involving land based aggregates were found these were also included. Information about the precise source of the aggregate in the structures showing AAR has seldom been available and even where it is known the material being worked today is not necessarily the same, so the aggregates tested here are of the same general type rather than being exactly representative of known reactive materials. Since it soon became apparent that the main reactive element in the aggregates was chert, the reactivity of chert rocks which could have been the sources of the chert in the sands and gravels were also investigated. The main techniques used were the monitoring of the expansion of mortar bars according to ASTM C227, of mortar bars with enhanced alkali levels and of concrete prisms. In addition evidence for the presence of reactive forms of silica was sought using X-ray powder diffraction and optical microscopy.

4.1 Mortar bar expansion tests

These tests were carried out according to ASTM C227 at a storage temperature of 38° using a high alkali Portland cement with an equivalent Na₂O content of 1.1%. This produces an alkali content in the mortar of about 6.5 kg of Na₂O

equivalent per cubic metre. Dilution of the test aggregate was with an inert basalt.

None of the materials from the UK which were tested have given deleterious expansions up to the present with one exception. The exception is a malmstone which is known to contain disordered silica. This material is quite different to the cherts found to have been attacked in concrete and is not used as an aggregate in concrete.

Under the standard conditions the ASTM C227 mortar bar test does not therefore appear to predict reactivity in the aggregate types known to have reacted in the field in the UK.

4.2 Mortar bars with enhanced alkali levels

In view of the lack of reactivity in the standard ASTM C227 test the expansion of chert at higher alkalinities has been investigated. The chert used was a black vitreous chert from the Monsaldale Beds of the Carboniferous limestone in Derbyshire. Two sets of experiments were carried out. In the first a high alkali (1.1% Na₂O equivalent) cement was used and the alkalinity of the mortar bars was increased by dissolving potassium hydroxide in the mix water. The second was similar but a very low alkali (0.25% Na₂O equivalent) cement was used. In neither series was there any expansion until the equivalent Na₂O level was about 1.5% by weight of cement (8.8 kg Na₂O/m³) and then the expansion rose rapidly. Using an enhanced level of alkali of 13.3% Na₂O in the mortar the chert was tested when it formed 100%, 50% and 10% of the whole aggregate. The results in Table 1 show that the expansion increased with increasing amounts of chert.

From this work a standard enhanced alkali level was decided on such that potassium hydroxide equivalent to 2% K₂O was added to the high alkali cement to produce a total equivalent alkali of 2.4% Na₂O equivalent or 14.2 kg Na₂O per cubic metre of mortar. Mortar bars containing this level of alkali were then used to test a selection of the chert rocks, quartzites and sands and gravels. The results are given in Table 1. Definite differences in reactivity between different samples of chert rock and between different sources of sands and gravels can now be seen.

The mortar bars containing sands dredged from off the South Coast and Thames Estuary and those containing sands and gravels from the Thames Valley deposits expanded by amounts which would be quite definitely classed as deleterious in concrete. Some of the cherts, in particular those from the limestone deposits, also produced large expansions. The Trent Valley sands and gravels and the sea dredged aggregates from off the Humber showed slight signs of reactivity but the other sea dredged samples and the cherts from the Lower and Upper Greensand deposits appeared unreactive. Too few samples have however been tested to draw generalised conclusions about differences in reactivity between samples of chert from the limestone and Greensand deposits.

4.3 Tests using concrete prisms

Although no reactivity is predicted in UK aggregates by the standard ASTM mortar bar test, expansion and cracking has been found in concrete specimens stored under similar conditions and containing similar amounts of alkali. This was first noticed at the UK Cement and Concrete Association in high

TABLE 1 EXPANSION OF MORTAR BARS WITH AND WITHOUT ENHANCED ALKALI LEVELS.
38°C STORAGE

Aggregate	% of test aggregate	% expansion			
		1 month	3 month	6 month	1 year
Sea dredged sand					
- Thames Estuary	100	0.03	0.18	0.24	
one of 2 samples tested					
- South Coast	100	0.03	0.26	0.27	
one of 3 samples tested					
- East Coast (Wash)	100	0.03	0.04	0.04	
- East Coast (Humber)	100	0.02	0.06	0.08	
- Bristol Channel	100	0.03	0.04	0.04	
Thames Valley sand	100	0.02	0.16	0.17	0.17
one of 4 samples tested					
Thames Valley gravel	100	0.03	0.10	0.10	0.11
Trent Valley sand	100	0.03	0.06	0.06	
one of 9 samples tested					
Trent Valley gravel	100	0.03	0.04	0.05	
Chert Rocks					
- Black vitreous chert from	100	0.03	0.15	0.18	0.18
Monsaldale Beds of the	50	0.03	0.06	0.09	0.09
Carboniferous limestone	10	0.03	0.03	0.04	0.04
Derbyshire					
- Portland cherty series,	100	0.03	0.10	0.10	0.10
Jurassic limestone					
- Chert from Lower Greensand,	100	0.02	0.03	0.03	0.03
Hythe Beds, Tilberstow Hill					
- Chert nodules from Upper	100	0.02	0.02	0.03	0.02
Greensand, Lulworth Cove,					
Dorset					
- Chert nodules from gravel	100	0.03	0.17	0.17	0.17
deposits in Oligocene,					
Bovey Tracey Beds					
Quartzite					
- Brown Cambrian quartzite	100	0.02	0.02	0.02	0.03
from Lickey, Warwickshire					
- Triassic quartzite from	100	0.02	0.02	0.02	0.02
Bunter Pebble Beds					

strength concrete cubes made for checking the accuracy of cube testing machines. A programme of tests using concrete specimens is now being carried out at BRE. Two series of specimens has been prepared. The first has a very high cement content (740 kg/m³) of the high alkali cement, giving an alkali content in the specimens of about 8 kg of Na₂O equivalent per cubic metre. The second series contain 560 kg/m³ of the cement producing about 6 kg of Na₂O equivalent /m³. Most of the tests so far have been carried out on one batch of Thames Valley sand and gravel although a few tests have also been carried out on a Trent Valley aggregate. The specimens used in the laboratory

tests are 75 x 75 x 200 mm prisms whereas for outdoors exposure larger 100 x 100 x 500 mm prisms are used. Storage is either in water at 20 or 38°C, in 100% relative humidity at 20 or 38°C or on an outdoor exposure site.

The results for specimens stored at 38°C are given in Table 2. No significant expansion has yet occurred in specimens stored at 20°C or on the exposure site. The results for the high cement content mixes containing the Thames Valley aggregate show a clear pessimum with a maximum expansion when 20% is present as a proportion of the whole aggregate. In the lower cement mixes only the specimens containing 20% Thames Valley aggregate in humid storage expanded to a significant extent. The Trent Valley aggregates did not show this pessimum effect, however, and the specimens containing all Trent Valley aggregate expanded to the greatest extent. The rate of expansion is also slower for the Trent Valley aggregate specimens.

TABLE 2 EXPANSION OF CONCRETE PRISMS AT 38°C. INERT AGGREGATE LIMESTONE

Aggregate	% of test aggregate	Na ₂ O _e kg/m ³	% expansion				
			1 month	3m	6m	9m	1 year
Thames Valley sand/gravel	10	8.14	0.010	0.025	0.037	0.062	0.085
	20		0.009	0.034	0.172	0.210	0.219
	30		0.007	0.034	0.154	0.168	0.168
	40		0.006	0.035	0.154	0.162	0.165
	60		0.008	0.026	0.036	0.035	0.036
	100	6.19	0.006	0.022	0.024	0.022	0.023
	10		0.005	0.010	0.017	0.019	0.017
	20		0.006	0.016	0.091	0.157	0.161
	30		0.004	0.011	0.019	0.022	0.021
	40		0.003	0.004	0.011	0.014	0.014
Trent Valley sand/gravel	60	8.14	0.003	0.003	0.009	0.010	0.009
	100		0.009	0.009	0.015	0.015	0.012
	10		0.006	0.018	0.027	0.035	0.037
	20		0.005	0.016	0.024	0.031	0.038
	30		0.008	0.022	0.035	0.046	0.054
	100	6.19	0.00	0.019	0.045	0.07	0.095
	30		0.005	0.013	0.015	0.017	0.016
	100		0.007	0.016	0.023	0.027	0.030

Where identical specimens were stored both in water and 100% relative humidity the expansion in the humid storage condition was generally greater.

Cracking is generally observed when the expansion exceeds about 0.05%.

4.4 Mineralogy of aggregates investigated

The mineralogy of the aggregates have been investigated using x-ray powder diffraction and optical microscopy. In addition the rates of dissolution in sodium hydroxide solutions have been measured.

4.4.1 X-ray diffraction before and after dissolution in sodium hydroxide solution

X-ray diffraction patterns of samples of the different chert rocks, the malmstone and cherts selected from the Thames Valley gravel have been obtained using a Guinier focussing camera. In addition diffraction patterns were taken after dissolution for periods of up to 1 year in sodium hydroxide solutions of 0.5, 1, 2 or 3 M strength at either 23°C or 38°C. This is based on a technique described by Gutteridge and Hobbs /6/ to investigate the mineral composition of beltane opal.

The rates of dissolution of the cherts were all quite similar and quite distinct from the malmstone. The rate for one of the cherts and the malmstone in 1 M NaOH at 38°C and 23°C is illustrated in Figure 1. It can be seen that about 30% of the malmstone is dissolved within a month at either 23 or 38°C and after that little more is dissolved. In contrast the rate of dissolution of the chert is much slower but is still increasing at 1 year. In 3 M solution up to 90% of some cherts is dissolved in one year in a similar steady manner. A reduction in temperature has a marked effect on the amount dissolved from the cherts.

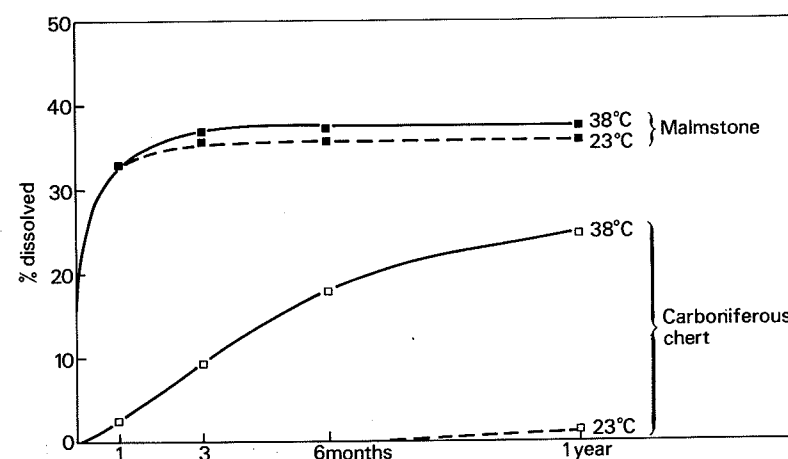


Fig 1. Rate of dissolution of malmstone and chert from carboniferous limestone in 1 M NaOH at 23°C or 38°C

The x-ray diffraction pattern of the malmstone showed strong, broad lines at about 4.05 Å and 4.25 Å. After one month in 1 M NaOH the broad lines had gone leaving a sharp line at 4.26 Å. This is consistent with the rapid dissolution of cristobalite and tridymite leaving quartz undissolved. In contrast the diffraction patterns of the cherts showed only quartz and calcite and there was no qualitative change after dissolution.

These results show that whereas in the malmstone there is a less - ordered, readily soluble form of silica, mineralogically similar to that found in beltane opal, in the cherts no such disordered form of silica is detectable.

We have found the detection limit of beltane opal interground with a chert to be 1% by X-ray powder diffraction and 5% by examination of the rate of dissolution.

4.4.2 Optical microscopy

In thin section, the cherts from the Carboniferous and Jurassic limestone, and from the Bovey Tracey Beds, which were shown to be reactive by the tests using mortar bars with enhanced levels of alkali had some characteristic differences from the cherts from the Upper and Lower Greensand which were not reactive. The former consisted typically of very fine grained even textured cryptocrystalline quartz, the crystallites varying from a size so small that it was impossible to measure optically up to about 20 microns. All the crystallites had a wavy extinction. Vein of chalcedony and calcite were present but those were not abundant. In the Greensand cherts on the other hand the silica was predominantly chalcedonic, coarsely textured and with abundant micro fossils such as foraminifera and sponge remains. Grains of glauconite and quartz sand were also present.

The cherts and flints which were found to be attacked by alkalis in deteriorated concrete were of the former kind, evenly textured, cryptocrystalline cherts although they did also tend to be stained brown by iron compounds, a feature not found in the samples of chert rock which were collected.

Taken together therefore the optical and x-ray examinations suggest that the principal reactive phase in the cases of AAR in the UK is cryptocrystalline quartz.

5. THE BSI WORKING GROUP ON TESTING THE ALKALI REACTIVITY OF AGGREGATES

This working group has been formed to consider whether there are tests for the alkali reactivity of aggregates which can be recommended as British Standard methods. The following are being assessed against aggregates of the types known to have reacted in concrete in the UK.

Petrological examination	ASTM C227 Mortar bar method
Gel pat test	Mortar bars with enhanced alkali content
ASTM C289 - Chemical method	Mortar bars stored in NaCl solution
German 'dissolution' method	Expansion of concrete prisms

The current thinking of the group favours a two tier system with a relatively rapid 'indirect' method as a screening test and a longer 'standard' method probably based on the expansion of concrete specimens.

6. DISCUSSION AND CONCLUSIONS

The optical and x-ray examinations of concrete affected by AAR and of aggregates of types found in such concrete give strong evidence that the principal form of silica to be attacked by alkalis in aggregates in the UK is cryptocrystalline quartz in flints and cherts. Since such flints and cherts occur widely in UK aggregates especially in sands and gravels from the Thames and Trent river valley and dredged from the Thames Estuary, South Coast and

Bristol Channel it is important to develop test methods which will reliably predict the alkali reactivity of such aggregates. The results so far of the assessment of possible test methods indicate that ASTM test methods, especially the C227 mortar bar test, can give misleading answers for UK materials but that tests using concrete specimens are more helpful. Tests using such concrete specimens have shown definite pessimum effects for some aggregates. The lack of expansion in mortar bars when concrete prisms containing the same amount of alkali and made with the same water/cement ratio and aggregate/ cement ratio crack and expand markedly is puzzling.

7. ACKNOWLEDGEMENT

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STANDARD ALKALI-REACTIVITY TESTING OF CARBONATE ROCKS FROM THE MIDDLE EAST AND NORTH AFRICA

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1. ABSTRACT

This paper arises from the experience of applying the standard rock cylinder test (ASTM C586-69) to variably argillaceous dolomites, limestones and dolomitic limestones from the Middle East and North Africa. Three case studies are presented, one involving an impure dolomite which exhibited delayed expansion in the rock cylinder test, and two similar rocks involving an impure limestone and a dolomitic limestone, from adjacent parts of one quarry, which exhibited unusually large and progressive contraction.

Comparisons are made between the rock cylinder test results and the petrological compositions and textures of the rock samples. The applicability of the rock cylinder test method for Middle Eastern and North African carbonate rocks is critically considered and an attempt is made to provide guidelines for the correct interpretation of rock cylinder test results for these materials.

Key Words: Carbonate, Alkali-Reactivity, Testing, Aggregate.

2. INTRODUCTION

Alkali-carbonate reactivity in concrete is very much less common than alkali-silica reaction. Nevertheless it remains a potential threat to concretes made using carbonate aggregates without a record of previous usage.

Since its discovery by Swenson in 1957 /1/ several distinct types of alkali-carbonate reaction have been identified /2/3/4/. These different types of reaction have been related to specific combinations of compositional and petrographic features of the rock involved and the effect of alkalies on the concrete and aggregate alike /5/6/.

Various tests for assessing potential alkali-carbonate reactivity have been used /7/8/9/10/11/. The ASTM C586-69 /12/ 'rock cylinder test' is similar to tests used by many research workers and involves the determination of the volume change of carbonate rocks when immersed in 1N NaOH solution at room temperature (say 20°C). The results from this test should not be considered as 'pass/fail' criteria for a rock proposed for use as concrete aggregate. However, they indicate whether further investigations should be carried out to determine the effect of aggregate prepared from the rock upon the dimensional change of a concrete.

The ASTM C586-69 test was originally described for North American carbonated rocks which sometimes exhibit significant expansion. For example, the argillaceous dolomitic limestone from Kingston, Ontario, has been found to produce rock cylinder expansions substantially in excess of 0.1% within two to three weeks /13/. The application of this test to dolomitic rocks from the Middle East and North Africa has shown that they frequently contract for a period of time, after which they sometimes start to expand /13/.

Lemish and Moore /9/ classified the carbonate rocks, with regard to their expansive tendencies in alkaline solutions, into four categories:

- Category I : Rocks which expand in excess of 0.5%
- Category II : Rocks which expand between nil and 0.5%
- Category III: Rocks which contract prior to expanding
- Category IV : Rocks which contract steadily