ALKALI-SILICA REACTIVITY IN CONCRETE FROM DHEKELIA, CYPRUS

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ABSTRACT

The history of the structural deterioration of Dhekelia jetty is traced from the first evidence of cracking to the complete breakup of the seaward end of the structure. The petrology of the aggregates used are described, and the chemically reactive material in the coarse aggregate described in detail. The mechanism of alkali-silica reactivity is discussed and analyses of the cement, aggregate and reaction products are presented.

The military jetty at Dhekelia is situated in Larnaca Bay on the south coast of the island of Cyprus. Since its completion in 1966 the jetty has been the subject of several investigations because of the unexpected and rapid deterioration that this particular concrete structure has undergone.

The structure consists of a reinforced concrete deck approximately 60 cm. thick supported on precast concrete piles about 2 metres above average high tide level. At the shore end of the jetty two ramps, one on each side of the main causeway lead down to sea level, and at the seaward end the decking divides forming a "Y" the arms of which also terminate in ramps leading down to sea level (Figure 1).

The abnormal rate of deterioration gave rise to concern soon after completion of the jetty, and in November 1969 the structure was examined and some repair work was carried out. This investigation revealed that both the upper and lower surfaces of the decking at the seaward end of the jetty were "soft and crumbly" to a depth of 5cm. In the course of the repair work which involved the removal of 7 to 8cm. of the decking surface large cavities 7 to 10cm. across were exposed and the concrete was found to be very soft and crumbly with the aggregate fragments very easily dislodged. Cracking was fairly widespread due it was thought to rusting of the reinforcement. A second examination of this structure was carried out in January 1971 with particular attention being paid to the piles and underside of the decking. Some of the piles were found to be severely eroded at the point of contact between the piles and the underside of the decking and a number showed evidence of cracking. The decking itself was most severely eroded on the underside of ramps 1, 3 and 4 (Figure 1). Ramp 1 had been eroded to a depth of 5 or 6cm. exposing the reinforcement but ramp 4 was the most severely eroded and in one small area this erosion had penetrated 15cm.

During July 1972 the jetty was re-examined by a small group from Queen Mary College and a collection of samples of the degraded concrete was made. Their examination produced evidence of further deterioration of the ramp surfaces with the removal of cement paste and exposure of aggregate, exposure of reinforcement and the development of a cavity in the centre of ramp 3. However, the most striking feature emphasising the structural deterioration since 1971 was the complete removal of a 3 metre length of the seaward extremity of ramp 4 to allow reapirs to be made. The original material had been thrown on the beach some hundred metres west of the jetty itself. It was noted that both prevailing wind and wave direction is from the south west and this may account for ramp 4 suffering the greatest structural damage.

Petrology of the Aggregate

The coarse aggregates used in the concrete of Dhekelia jetty are natural river or beach gravels containing a wide variety of sedimentary and igneous rock types. Grading of the coarse aggregate appears uniform in the samples collected and typically has a maximum grade size of 20mm, although one core taken from the decking had a maximum grading of approximately 30mm. The majority of pebbles appear well-rounded and many exhibit a thin natural weathering rim when examined in cut sections. In the smaller grade sizes an increasing proportion of the fragments have irregular broken faces or are angular, and on average between 5 and 10 percent of coarse aggregate fragments as a whole are angular in shape.

Although all the samples of concrete examined contain a similar variety of rock types, there is considerable variation in the proportions present in the different samples. Table 1 below compares the modal composition of coarse aggregates in a core section cut from sound decking (sample A) with a similar mode made on a sample taken from the broken pieces of ramp 4 (sample B).

Table 1. Modal Composition of Coarse Aggregates, Volume Percentages

Rock Group (1)	Rock Type	Sample A	Sample B
Gritstone	Grey, cream & red sandstones	20	25
	Fine grained calcitic sandstones	10	25
Gabbro	Dolerite	30	35
	Gabbro	15	5
Flint	Grey, red & brown cherts	20	2
Quartzite	Vein quartz	1	5
	Others	4	8

The fine aggregate in all the samples examined is composed of similar rock types to those of the coarse aggregates, though quartz grains are an important constituent group in this material. A typical modal analysis for the fine aggregate is given in Table 2.

Table 2. Modal composition of Fine Aggregate, Volume Percentages

Rock or Mineral Type	Comment	Volume Percent
Basic Igneous Rocks	Dolerite and similar rock types to the coarse aggregate	45
Sandstones	Similar types to coarse aggregate	3
Cherts	Red and brown similar to coarse aggregate	5
Quartz	Subrounded and angular grains	35
Calcite	Including shell material	5
Feldspar	-	2
Others	-	5

The rock materials predominate in the coarser fractions of the fine aggregate, while quartz is the dominant mineral for grains of 1mm. diameter and smaller. The majority of grains are angular or subangular in shape and angularity appears to increase in the smaller grade sizes.

It is difficult to determine the original percentage void in the severely decayed concrete samples but in relatively sound samples rounded voids up to 5mm. diameter are fairly common and total void space is estimated at between 3 and 5 percent.

The Reactive Aggregate Particles

The nature of the deterioration of the concrete samples from Dhekelia includes cracking, development of reactions rims, silica gel and other features which are clearly indicative of the alkali-silica reactivity as described by Stanton (2), Idorn (3) and many others.

These chemical reactivity features are always associated with the cream-coloured calcitic sandstones referred to in Tables 1 and 2. These sandstones are somewhat variable in composition and are composed of varying proportions of diatom tests cemented together with varying amounts of secondary silica and calcite. In thin section these particles are seen to be partly composed of interlocking crystalline anisotropic quartz grains. The siliceous diatom tests are however, opaline silica (4) and these opaline areas appear to be the initial sites of reaction. The wide variation in the amounts of diatomaceous material, cementing silica and calcite appears to be reflected in the chemical reactivity of different aggregate particles, in general those with the highest proportion of diatomaceous material and calcite cement exhibit the most extreme features of chemical reactivity.

In broken pieces of concrete and on cut surfaces the most obvious features indicative of alkali-silica reactivity are the appearance of dehydrated silica gel, the extensive fracturing of the concrete with cracks which are filled with white dehydrated gel and the development of darker reaction rims up to 2mm. wide around the margins of the cream calcitic sandstone fragments. The dehydrated gel is readily identified by infrared spect scopic analysis since certain absorption bands for silica gel and calcium carbonates in the 650 to 1600 wavenumber region are characteristic of these materials. The dehydrated gels examined in this work were all heavily carbonated, but in addition to calcite, aragonite is also present, presumabl having formed either in a metastable state or under conditions of high pressure (5).

In thin section the dehydrated gel is seen to have contracted and now occupies only parts of each crack system. Where a fracture system cuts through a reactive aggregate particle the calcite cement of the particle itself appears to have been leached away leaving an irregular zone typically about 1mm. wide entirely free of calcite bordering the crack.

In thin section the reaction zones at the margins of reactive particles can be seen to be composed of several different light and dark zones which appear to grade into each other. Typically a system of microfractures develops within this zone parallel to the margins of the aggregate though sometimes cracks perpendicular to the rim develop instead, these are particularly noticeable where the rims are wide.

Chemical Data

The reaction between reactive silica and alkalis in cements and concretes leads to the formation of an alkali silica gel of an indefinite composition which sets up expansive changes leading to the disruption of the concrete (6) (7). Analyses 1 and 2 in Table 3 reflect the variation in composition between different reactive aggregate fragments in the Dhekelia samples. In general terms the major chemical variation reflects the varying proportions of quartz and calcite in these particles. The analyses also show that these reactive rocks contain a small percentage of alkalis. The small amounts of chlorine in a number of the analyses suggests that the sea water also contributes some sodium ions to the concrete. The cement itself (analysis 7) contains alkalis but the amounts are comparable with those in ordinary portland cements.

A comparison of the chemical analyses of a reaction rim (analyses 3 and 4) with the aggregate composition is striking. The most important changes in the rim zone are the marked increase in silica, the reduction in alkalis and lime, and the variation in magnesia. There is also a striking difference between the composition of the reaction rim and the silica gel reaction product (analyses 5 and 6). The high lime figures and lower silica reflect the carbonated nature of the gel in these samples, but the low magnesia and high but variable alkali figures contrast with those of the rim zone. Water, carbon dioxide and other volatiles cannot be determined by electron probe microanalysis, but the totals given for

Table 3. Analyses of Reactive Aggregate, Reaction Products and Cement

	1	2	3	4	5	6	7
SiO_2	64.22	72.69	84.76	80.65	51.42	53.04	21.65
TiO_2	0.06	-	-	-	-	-	-
Al_2O_3	0.98	1.71	1.49	2.48	0.22	0.30	3.54
Fe_2O_3 } FeO	0.53	1.96	1.00	1.61	L 0.1	L 0.1	2.79
MnO	0.03	-	-	-	-	-	0.08
MgO	1.11	2.32	1.17	2.40	L 0.05	L 0.05	2.07
CaO	15.86	3.83	2.94	2.34	29.98	22.10	64.20
Na_2O	0.61	1.14	L 0.1	0.34	1.07	7.41	0.39
K_2O	0.26	0.85	0.3	0.62	0.45	0.70	0.56
Ig loss	15.74	-	-	-	-	-	-
S	-	2.21	0.23	L 0.03	L 0.04	L 0.04	-
Cl	-	0.59	0.58	0.78	1.93	1.06	-
	99.40	87.30	92.57	91.25	84.25	84.80	95.28

L = less than

\- = No data

1. Bulk chemical analysis of a reactive aggregate particle.
2. Electron probe analysis of the central portion of a reacted particle.
3. Electron probe analysis of the inner part of the reaction rim associated with the particle referred to in 2 above.
4. Electron probe analysis of the outer part of the same reaction rim.
5. Electron probe analysis of silica gel from a fracture.
6. Electron probe analysis of silica gel 2mm. from analysis 5.
7. Bulk chemical analysis of Cyprus cement.

analyses 2 to 6 clearly indicate a general increase in volatile content in the rim zone and the gel by comparison with the aggregate particle (analysis 2).

Discussion

The work of Powers and Steinour (8) suggests that calcium ions may be important in influencing the alkali-silica reaction in concrete. The observations made on the reactive Dhekelia samples suggests that both calcium carbonate from the aggregate and calcium from the cement paste are involved in the reaction process. Calcium carbonate appears to be removed from the aggregate during some stage of the reaction process, and the carbonated nature of the gel suggests further calcium may be obtained from the cement itself. Certainly the calcium levels indicate that some calcium may be incorporated in the gel thus forming an alkali-lime-silica gel and/or an additional calcium rich phase is present. A comparison of the alkali and silica concentrations for the aggregate, reaction rim and gels indicates that the reaction involves high local silica concentrations but that alkali concentrations are initially very low and only appear to increase as the gel develops and becomes more fully hydrated as it moves away from the reaction site.

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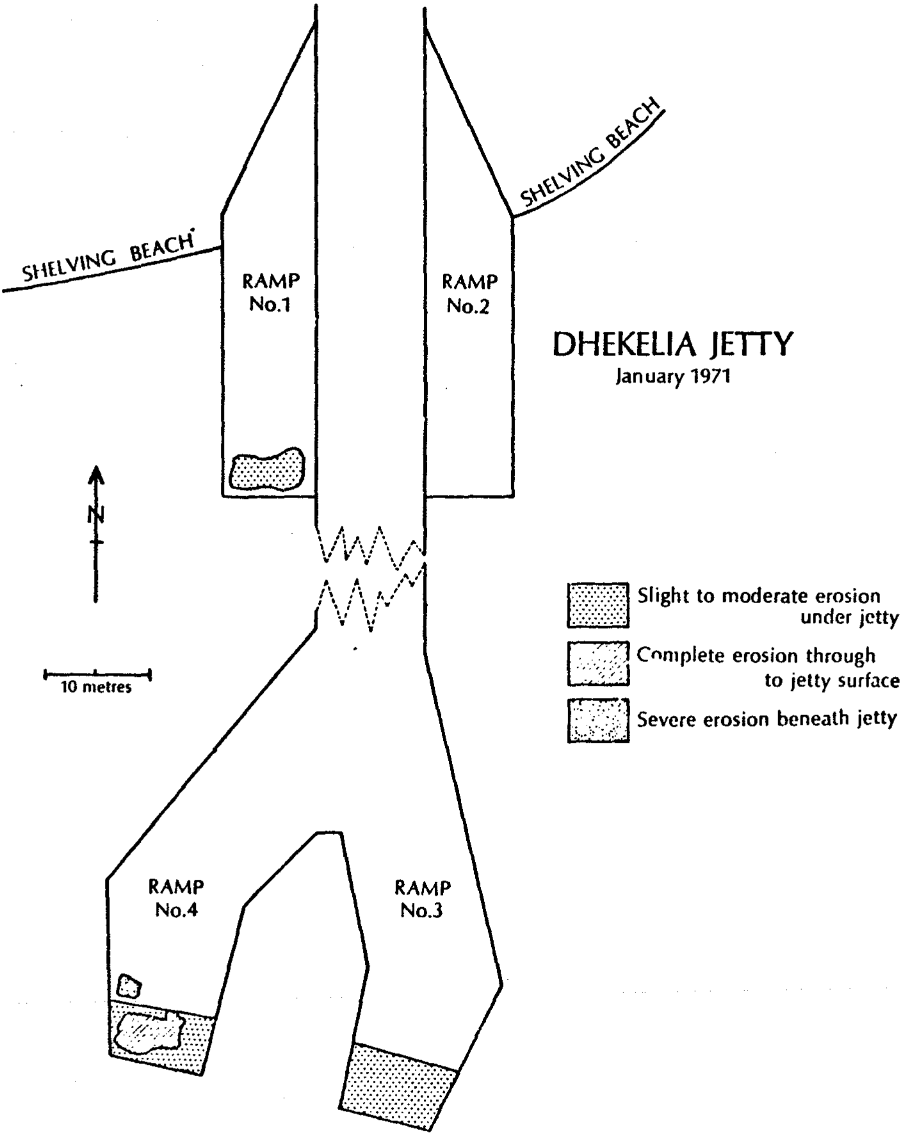
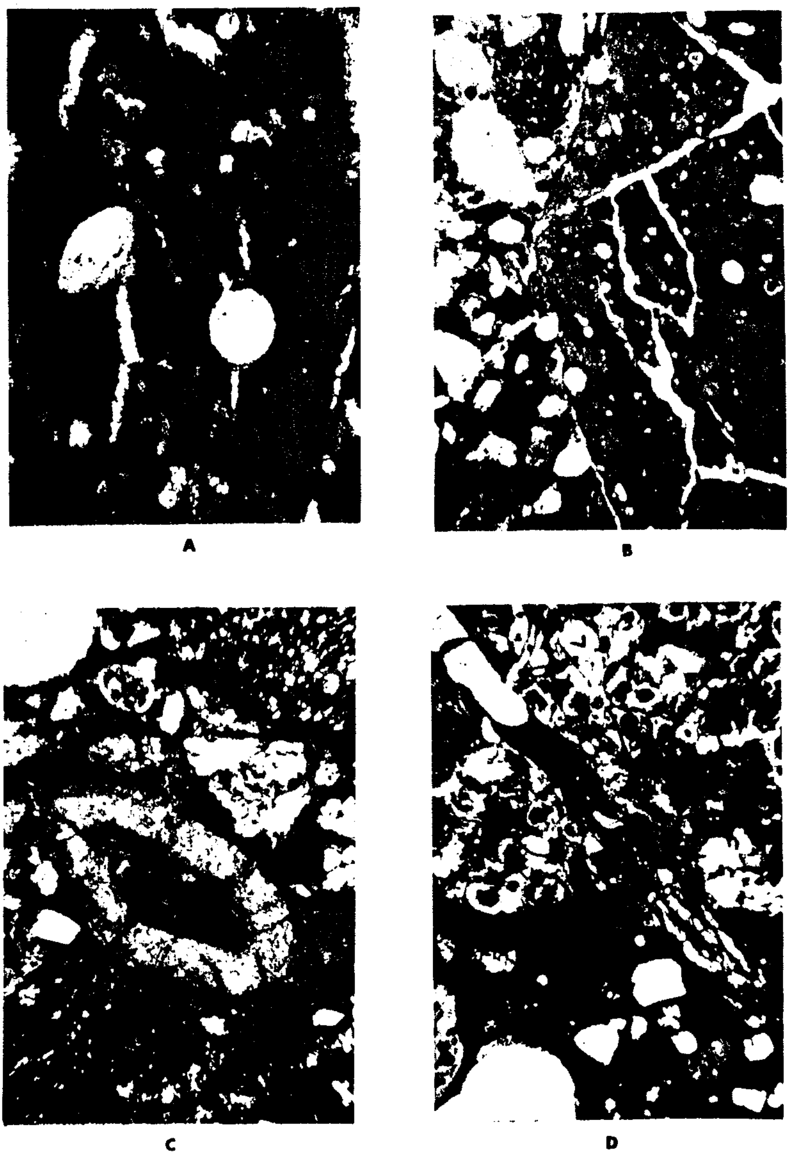

DHEKELIA JETTY
January 1971
SHELVING BEACH
SHELVING BEACH
RAMP No.1
RAMP No.2
RAMP No.3
RAMP No.4
N
10 metres
Slight to moderate erosion under jetty
Complete erosion through to jetty surface
Severe erosion beneath jetty

Figure 1



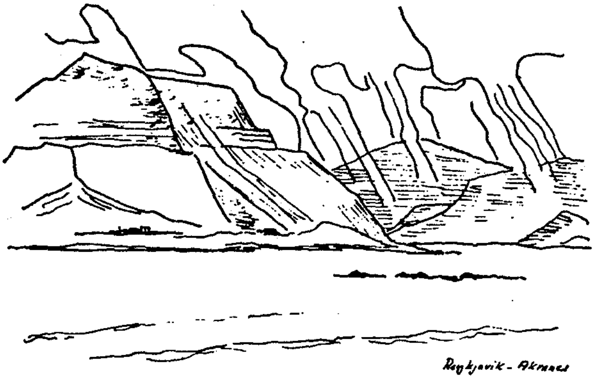
A Development of gel filled cracks in opaline calcitic aggregate.

B Development of a silica enriched rim and microcracks in reactive aggregate fragment.

C Wide siliceous rim surrounding reactive aggregate (analyses 2,3 and 4).

D Microcrack in reactive aggregate partly filled with gel. Zone surrounding the crack (L) leached free of calcium carbonate.

Width of photomicrographs B C & D = 2mm, A = 0.2mm



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