THE INTERACTION OF ALKALIES WITH DOLOMITE AND QUARTZ IN EXPERIMENTAL CONCRETE SYSTEMS

A. B. Poole and P. Sotiropoulos
Queen Mary College, University of London, London E.1.

ABSTRACT

Dolomitic limestones from Bahrain, Arabian Gulf and quartz sand have been used as aggregate in experimental concretes which were specially prepared to investigate the detailed mechanisms which produce non expansive alkali-carbonate, and alkali-silica reactivity in specimens stored at 95 percent relative humidity for periods up to 10 months and temperatures up to 50°C. Scanning electron microscopy has been used to examine the features of the reacting interface and chemical and electron probe microanalysis have been used to investigate the distribution of Na, K, Ca, Mg, Si, SO_3 and Fe ions in the reaction zone. Petrographic and chemical data are presented indicating that the reaction zone may be subdivided into sub-zones in the cement paste and aggregate. The mechanisms for the initial development, progress and eventual slowing down of the dedolomitization process are described and the factors which influence it are discussed.

Introduction

The great majority of carbonate rocks are for practical purposes chemically inert and if physically suitable make excellent concrete aggregates. However, some fine grained dolomitic limestones have been described which are chemically unstable in ordinary portland cement concrete. Certain fine grained argillaceous dolomites described by Swenson (1), Swenson and Gillott (2) and Gillott (3) react with the alkalies in the cement paste causing expansion of the concrete. More recently dolomitic aggregate materials obtained from geologically young strata in Bahrain (4) and certain other parts of the Middle East have been shown to develop clear reaction zones at the cement/aggregate interfaces (Figure 1). These reaction zones do not appear to be expansive though their true effects on durability are sometimes masked by sulphate contamination of the concrete in certain case study examples.

Hadley (5, 6) in 1961 and 1964 reviewed the types of alkali-carbonate reactivity in concretes and proposed reaction mechanisms to explain the experimental observations made. The principal reaction is one of dedolomitization which may be written as

$$\mathrm{Ca\,Mg\,(CO_3)_2 + 2\,M\,OH - Mg\,(OH)_2 + Ca\,CO_3 + M_2\,CO_3}$$

where M may represent Na, K or Li.
The alkali carbonate produced from the reaction will in turn react with the hydration products of the cement thus regenerating the alkalies and permitting continued reaction with the dolomite

$$\mathrm{M_2\,CO_3 + Ca\,(OH)_2 - 2\,M\,OH + Ca\,CO_3}$$

The observed increase in silica concentration in the rim zone is explained by Hadley as due to silicate ions in solution reacting with the brucite formed in the dedolomitization reaction. Hadley also suggests that the alkali carbonate formed diffuses into the paste to react with calcium sulphoaluminate hydrates to form calcium carboaluminate hydrate releasing sulphate ions which diffuse back into the cement paste "ahead of the advancing carbonate front while the alkalies are regenerated and diffuse again into the rock."

In order to study the details of alkali-carbonate reaction mechanisms of this type and their affect on carbonate rocks from the Middle East a series of samples of limestones, dolomites and dolomitic limestones were selected from a collection of rocks made in Bahrain, Arabian Gulf. Two dolomites were chosen from this series and used in the detailed study of the reactions and their development with time. A pure limestone from Bahrain of similar grain size was used as a control in the experiments.

Figure 1. Well developed rims round dolomitic limestone aggregate fragments in concrete from Benghazi, Libya. Width of photograph equivalent to 120 mm.

Experimental Method.

Petrographic examination of the selected samples show sample 13 to be fine grained with individual grains averaging 0.01 mm diameter and with a porous texture. Individual voids are irregular and range up to 1 mm across though more typically they have diameters of about 0.3 mm. Sample 19 by contrast is coarser grained with grains averaging 0.025 mm diameter though they range in size from about 0.05 to 0.005 mm. The intergrain boundaries are flat rather than interlocking in sample 19, but grains are too small to be clearly resolved in sample 13. The water absorption of the two samples was determined according to B.S. 812 (6) and gave values of 10.0% for sample 13 and 2.0% for sample 19, the relative densities were 2.15 for 13 and 2.68 for 19. The typical textural features of sample 19 are shown if figure 2 and the aggregate particle in figure 5 is typical of sample 13.

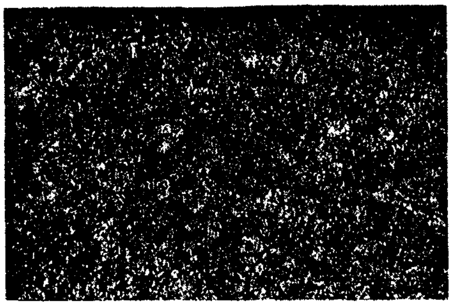

Figure 2. Photomicrograph of dolomite sample 19. Transmitted plane polarised light width of photograph 0.75 mm

Chemical analyses of these samples (Table 1) confirm infrared and diffraction analyses showing these rocks to be pure dolomites containing only traces of other materials. Infrared analysis shows the acid insoluble fraction (Table 1) to be principally composed of attapulgite clay together with a little quartz.

TABLE 1

Partial Analyses of Rock Samples

	Sample 13	Sample 19
CaO	29.66	30.25
MgO	21.57	21.85
Acid insoluble Residue	0.92	0.49

The rock material was crushed and sieved to provide fragments between 2.5 and 5 mm diameter, and these together with sand were mixed in the proportion one part by weight of aggregate to one part cement, with a water cement ratio of 0.35. The aggregates were mixed in the proportion one part pure quartz sand to two parts by weight of dolomitic fragments.

The analysis of the cement used is given in table 2.

TABLE 2

Analysis of Ordinary Portland Cement Weight %

SiO_2	21.3
TiO_2	0.33
FeO	2.49
Al_2O_3	5.35
MnO	0.06
CaO	65.8
MgO	1.3
Na_2O	0.21
K_2O	0.62
SO_3	2.35
P_2O_5	0.19
	100.00