Appendix E
Alkali-Carbonate Rock Reactions

E-1. General Statement.

The results of studies that have been reported indicate that four types of alkali-carbonate rock reaction may be recognized in concrete. A thorough review of research through 1964 is contained in paragraph E-4 of this manual (Highway Research Board 1964).* It is possible that future work will show that some of these are merely different manifestations of the same reaction, shown by different rocks under a variety of circumstances. The four types of reactions are discussed in the following subparagraphs:

a. Reactions involving nondolomitic carbonate rocks. Some rocks which contain little or no dolomite may be reactive (Mather et al. 1963; Buck 1965). The reaction is characterized by reaction rims which are visible along the borders of cross sections of aggregate particles. Etching these cross-sectional surfaces with dilute hydrochloric acid reveals that the rims are "negative" rims, i.e. the reaction rim zone dissolves more rapidly than the interior of the particle. The evidence to date indicates that the reaction is not harmful to concrete and may even be beneficial.

b. Reactions involving dolomite or highly dolomitic carbonate rocks. The reaction of dolomite or highly dolomitic aggregate particles in concrete has been reported (Tynes et al. 1966). The reaction was characterized by visible reaction rims on cross sections of the aggregate particles. When these cross-sectional areas of aggregate particles were etched with acid, the rimmed area dissolved at the same rate as the nonrimmed area. No evidence was reported that this reaction was damaging to concrete.

c. Reactions involving impure dolomitic rocks. The rocks of this group have a characteristic texture and composition. The texture is such that larger crystals of dolomite are scattered in and surrounded by a fine-grained matrix of calcite and clay. The rock consists of substantial amounts of dolomite and calcite in the carbonate portion, with significant amounts of acid-insoluble residue consisting largely of clay. Two reactions have been reported with rocks of this sort, as follows:

(1) Dedolomitization reaction. This reaction is believed to have produced harmful expansion of concrete (Hadley 1961). Magnesium hydroxide, brucite ($Mg(OH)_2$), is formed by this reaction; its presence in concrete which has expanded and which contains carbonate aggregate of the indicated texture and composition is strong evidence that this reaction has taken place.

(2) Rim-silicification reaction. This reaction is not definitely known to be damaging to concrete, although there are some data which suggest that a retardation in the rate of strength development in concrete is associated with its occurrence. The reaction is characterized by enrichment of silica in the borders of reacted particles (Bisque and Lemish 1958). This is seen as a positive or raised border at the edge of cross sections of reacted particles after they have been etched in dilute hydrochloric acid. Reaction rims may be visible before the concrete surfaces are etched. Fortunately, carbonate rocks that contain dolomite, calcite, and insoluble material in the proportions that cause either the dedolomitization or rim-silicification reactions are relatively rare in nature as major constituents of the whole product of an aggregate source.

E-2. Criteria for Recognition of Potentially Harmfully Reactive Carbonate Rocks

These criteria serve to indicate those dolomitic carbonate rocks capable of producing the dedolomitization or rim-silicification reaction. Since the reactions generated by some highly dolomitic or by some nondolomitic carbonate rocks are not known to be harmful to concrete, no attempt is made to provide guides for recognition of these rocks at this time.

a. Petrographic examination. When petrographic examinations are made according to ASTM C 295 (CRD-C 127) of quarried carbonate rock or of natural gravels containing carbonate-rock particles, adequate data concerning texture, calcite-dolomite ratio, the amount and nature of the acid-insoluble residue, or some combination of these parameters will be obtained to recognize potentially reactive rock. Rocks associated with observed expansive dedolomitization have been characterized by fine-grain size (generally 50 micrometres or less) with the dolomite largely present as small, nearly euhedral crystals generally scattered in a finer-grained matrix in which the calcite is disseminated. The tendency to expansion, other things being equal, appears to increase with increasing clay content from about 5 to 25 percent by weight of the rock, and also appears to increase as the calcite-dolomite ratio of the carbonate portion approaches 1:1.

b. Testing. Samples of rock recognized as potentially reactive by petrographic examination will be tested for length change during storage in alkali solution in accordance

* References cited in this appendix are given in Appendix A of this EM.

with ASTM C 586 (CRD-C 146). Rock characterized by expansion of 0.1 percent or more by or during 84 days of test by ASTM C 586 should be classified as potential reactive.

c. Service record. If adequate reliable data are available to demonstrate that concrete structures containing the same aggregate have exhibited deleterious reactions, the aggregate should be classified as potentially reactive on the basis of its service record.

E-3. Control of Alkali-Carbonate Reaction

The application of engineering judgment will be required in making the final decision as to which rocks are to be classified as innocuous and which are to be classified as potentially reactive. Once a rock has been classified as potentially reactive, the action to be taken should be as indicated in the following subparagraphs.

a. Reactive aggregate. Avoid use of aggregate of rock classified as potentially reactive by appropriate procedures such as selective quarrying.

b. Other control methods. If it is not feasible to avoid the use of rock classified as potentially reactive, then specify the use of low-alkali cement and pozzolan, the use of the minimum aggregate size that is economically feasible, and dilution so that the amount of potentially reactive rock does not exceed 20 percent of the coarse or fine aggregate or 15 percent of the total if reactive material is present in both.

c. Aggregate source. If it is not practical to enforce conditions in subparagraphs a or b, then the aggregate source that contains potentially reactive rock shall not be indicated as a source from which acceptable aggregate may be produced.